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**CO-ORDINATED RESEARCH PROJECT ON
ASSESSMENT OF LEVELS AND HEALTH-EFFECTS OF
AIRBORNE PARTICULATE MATTER IN MINING, METAL
REFINING AND METAL WORKING INDUSTRIES USING
NUCLEAR AND RELATED ANALYTICAL TECHNIQUES**

Report on the First Research Co-ordination Meeting (RCM)

Vienna, Austria

20 - 24 October 1997



INTERNATIONAL ATOMIC ENERGY AGENCY

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Report on the First Research Co-ordination Meeting (RCM)

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NAHRES - 42, IAEA, VIENNA (1998)

A report prepared by the

**Section of Nutritional and Health-Related Environmental Studies
Division of Human Health
Department of Nuclear Sciences and Applications
International Atomic Energy Agency
P.O. Box 100
A-1400 Vienna, Austria**

*Single copies of this report are available cost-free
on request from the above address*

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SUMMARY REPORT

1 INTRODUCTION

The increased awareness of occupational health, hygiene and safety in recent years has resulted in improvement of working conditions and in reducing workers' exposure to some toxic agents. However, substantial hazards remain, the number of cases of occupational illness due to these hazardous exposures is still high, and new cases will continue to occur if there are no improvements. During the past years investigations have revealed a number of examples of unreported occupational diseases. New problems have appeared with changes related to energy development, biotechnology, electronics, chemicals and other industrial activities. There is an increasing tendency to develop essentially ambient, but also biological limits and to develop methods of ensuring their implementation, thereby preventing health damage from exposure to toxic chemicals. Aspects of monitoring include providing information to help achieve compliance with standards, validating that compliance and accumulating information for later review of the standards.

Nuclear and related analytical techniques (NRATs) have important applications in the study of workplace monitoring associated with mining, refining and metal working industries, providing data that are useful in the assessment of the possible health effects of such human activities. Toxic heavy metals, together with other trace elements that may have harmful effects, can be determined in airborne particulates and in human tissues by neutron activation analysis (NAA), using neutrons from a research nuclear reactor or neutron generator, by other forms of activation analysis (e.g. with photons), by particle induced X-ray emission (PIXE) analysis, by X-ray fluorescence (XRF) analysis and by inductively coupled plasma-mass spectrometry (ICP-MS) analysis.

For many years the International Atomic Energy Agency (henceforth "the Agency") has been supporting co-ordinated research within the framework of a Project on Environmental Pollution Monitoring and Research Using Nuclear and Related Analytical Techniques. The objective of this work is to demonstrate the applicability of nuclear and related analytical techniques (mainly NAA, XRF, PIXE and ICP-MS) in studies of non-radioactive pollutants that may impact on human health, giving emphasis to the solution of problems that have been identified to be of high priority in national and international programmes for sustainable development. In view of the fact that the highest concentrations of toxic agents, in particular metals and their compounds (and therefore also the most important health effects), are generally observed in the workplace environment, the Agency started in late 1996 a Co-ordinated Research Project (CRP) on "Assessment of levels and health-effects of airborne particulate matter in mining, metal refining and metal working industries using nuclear and related analytical techniques". The objectives of the CRP are to: (1) improve competence for research on workplace monitoring in terms of proper sampling and analytical procedures, (2) obtain relevant and reliable data on sources and levels of workplace pollution in various countries, (3) promote a better understanding of methods for the interpretation of such data including occupational health studies, and (4) encourage closer collaboration between analytical scientists and researchers in the field of occupational health in the countries concerned.

The first Research Co-ordination Meeting (RCM) for participants in the CRP was held at the Agency's headquarters in Vienna. The list of participants is given in Annex 1 and the agenda in Annex 2.

Information on individual participant's work for the first year and plans for the second year of the CRP are given in Annex 3. Progress achieved so far and plans for implementation of the CRP, was presented in each country's report. These reports are reproduced in Annexes 4-13.

The following summary report restates some of the principal features of the CRP and provides additional detail - based on the discussions held during this RCM - on how the CRP will be implemented.

2 THE CORE PROGRAMME

2.1 Overall Objectives of the CRP

The highest concentrations of toxic agents, in particular metals and their compounds (and therefore also the most important health effects), are generally observed in the workplace environment. The objective is to demonstrate the applicability of nuclear and related techniques (NRAT) in studies of pollutants that may impact on human health, giving emphasis to the solution of problems that have been identified to be of high priority in national and international programmes for sustainable development.

2.2 Specific Research Objective

The CRP will focus on the use of nuclear and related analytical techniques for the following kinds of studies:

- (1) Strategies and techniques for sampling of workplace airborne particulate matter (APM) and of human tissues and body fluids (hair, blood, etc.) sampling of exposed and non-exposed persons;
- (2) Development of suitable analytical procedures for analysis of such types of samples;
- (3) Workplace and personal monitoring of APM in the mining, refining and metal working industries, and the health effects of such exposure;
- (4) Tissue analyses of the workers so exposed for biological monitoring and the health effects studies.

Studies of the levels and health effects of organic and organo-metallic constituents, and naturally occurring radionuclides (e.g. relating to exposure to uranium, thorium and their daughter products in mining and refining) may also be included, but will not be the single main focus of the CRP.

3 THE SUPPLEMENTARY PROGRAMME

The supplementary programmes identified by the various participants are provided below. They are complementary to the primary objectives of the second phase of the CRP of some of the individual participating countries.

- Determination of the various chemical states of some of the identified constituents (speciation) and the determination of the solubility in body fluids;
- Determination of enriched levels of pollutants in soil, sediment, water and food;
- Comparison and validation of various sampling devices.

4 EXPECTED BENEFITS OF THE PROGRAMME

Overall, it is expected that the CRP will:

- (1) Improve competence for research on workplace monitoring in terms of proper sampling and analytical procedures;
- (2) Obtain relevant and reliable data on sources and levels of workplace pollution in various countries;
- (3) Promote a better understanding of methods for the interpretation of such data including occupational health studies;
- (4) Obtain information on normal background levels of potential pollutants in humans;
- (5) Contribute to the systematic collection of data on possible toxic constituents;
- (6) Provide a comparison of threshold limit values (TLVs) in the working environment as allowed by the various participating countries and other international and national standards or regulations where available. This could lead to a working document for national authorities (South Africa will provide the compiled report at the next meeting);
- (7) Demonstrate the use of NRATs in health related studies;
- (8) Provide new information on the behaviour, interpretation and optimisation of possible pollutants in the workplace environment;
- (9) Encourage closer collaboration between analytical scientists and researchers in the field of occupational health in the countries concerned.

5 TECHNICAL ASPECTS

5.1 Sampling

5.1.1 Airborne Particulate Matter (APM)

- Monitoring should be performed for various workplaces in the mining and mineral processing industry; this could involve various processing plants and waste dumps. Sites for background measurements should be included.
- A representative group of workers should be monitored. Definitions based on the number of individuals concerned can be found in various documents. Typical guidelines are provided in:
 - Developments in Workplace Aerosol Sampling, Analyst, September 1996, Vol. 121 (1233-1239).
 - The South African guidelines issued by the Government Mining Engineer (GME), which could serve as a common base for the participants in the CRP.
- The use of personal samplers and area samplers should be envisaged.
- Blank contributions from support filters are not regarded as serious. However, care should be taken by evaluation of the background data obtained.
- Detailed information on personal samplers and air pumps is provided in the South African GME document. The following instruments are used by some of the participants.

Country	Particle size of RAD (AMAD) Type	Sampler Type	Pump Type	Filters Type
CZR	< 2,5 & 10 μm	SKC	SKC	?
IND	< 10 μm	Home made	Home made	?
RUS	< 2,5 & 10 μm	Aspirator 822	AC-1	AFA XA-20
SAF	< 7 μm	Gillian	Gill-Air	Organic membrane
SLO	< 5 μm	Casella	Casella	Polycarbonate

Action requested:

- The IAEA to explore the possibility to purchase and distribute samplers with 2.5 μm AMAD cut-off particle size and appropriate pumps to all participants. The estimated costs per unit (samplers & pump) is about US\$ 1000.
- To incorporate the "Gent"-sampler in the sampling programme. The IAEA will evaluate the possibility to purchase and distribute it to all participants.

5.1.2 Biological Samples

Hair Samples

The reference information on sampling can be obtained in the report NAHRES-7, Vienna, 1991: Assessment of Environmental Exposure to Mercury in Selected Human Populations.

Blood and Urine Samples

The reference information on sampling can be obtained in: J. Trace Elements Med. Biol., Vol. 10, 103-127 (1996).

Nail Samples

The reference information on sampling will be provided the participant of CZR. It is recommended to use as the first wash a solution of ~1% by volume of distilled water and Triton X-100. Washing should be performed in an ultrasonic bath for five minutes. Toe-nails are recommended, but care should be taken as workers could collect pollutants by walking bare-foot. Care should also be taken in the evaluation of the total body burden due to possible external contamination.

Saliva

Possible contamination from dental treatments with amalgam, gold, plastics and ceramics should be considered in the data evaluation. However, the matrix is not recognised for general monitoring of trace elements.

Sweat

This is not recommended for routine application to determine the body burden of elemental pollution.

5.1.3 Sampling Frequency

Urine

- To be collected at the end of a five day work shift and before the start of the next shift.
- Collection of samples should be performed at the time of a medical examination.
- Collection should be done under as clean as possible circumstances.

Blood

It is recommended to perform the sampling of blood at the same time of urine sampling. This could be done during medical examination as a (medical) qualified person is required for the blood sampling.

5.1.4 Storage of Samples

Storage should be done according to IUPAC recommendations. The reference information on sampling can be obtained from, J. Trace Elements Med. Biol., Vol. 10, 103-127 (1996).

5.1.5 Standardisation of Sampling

It is recommended that the individual participating countries apply their own methods for sampling. They should, however, include a blank procedure. The blank procedure for blood could be the sampling of triple distilled water (use quartz glassware) or "Milli-Q" purification equipment. Albumin serum solution should also be considered as a blank sampling solution.

The provision of standard sampling devices by the IAEA is not regarded as practical.

5.2 Analysis

No special advice is required on analytical techniques, sample and sub-sample preparation, or any other aspects of the analysis programme.

Priority samples and analytes to be studied in individual countries are presented in chapter 4.

The appointment of "reference analytical laboratories" to assist in the CRP is not regarded as a necessity for the time being.

5.3 Data Processing and Interpretation

The use of commercially available data bases and/or spread-sheets is recommended for the manipulation of the data obtained.

The following programmes used by the various participants are *Excel*, *Quattro Pro*, *Minitab*, *Origin*, *S+*, *SAS*, *Statgraphics* and *SPSS* (the most frequently used ones are printed in italics).

IFCC software is recommended for the calculation of reference limits, while IUPAC software should be used for the determination of coverage intervals.

No specific effort will be made to apply central data processing of all data obtained by the participants.

Action requested: The IAEA should evaluate the possibility to purchase and distribute these programs amongst the participating countries.

5.4 Anticipated Contributions and Priorities in the Second Year of the Programme

The participants evaluated the anticipated contributions for the following phase of the CRP. It is emphasised that this could change due to changing circumstances during the duration of this phase, but in general should be achievable. The data are compiled hereunder.

Country	APM	Human Tissue	Human Body Fluids	Techniques	Monitoring	Health Studies
BRA	Yes	Yes	Yes	INAA, AAS, XRF	Yes	Yes
CPR	Yes	Yes	Yes	INAA, PIXE, SRXRF	Yes	Yes
CZR	Yes	Yes	Yes	INAA, PIXE	Yes	?
IND	Yes	Yes	Yes	INAA, ICP-AES, XRF	Yes	?
INS	Yes	Yes	Yes	INAA, RNAA, AAS	Yes	Yes
KEN	Yes	Yes	Yes	TXRF, PIXE, AAS	Yes	Yes
POR	Yes	Yes	Yes	INAA, PIXE	Yes	Yes
RUS	Yes	Yes	No	INAA, XRF, AAS	Yes	Yes
SAF	Yes	No	No	INAA, RNAA	Yes	Yes
SLO	Yes	Yes	Yes	INAA, (T)XRF	Yes	Yes

Country Priorities

BRA	Several elements in APM and human tissues
CPR	Cr, Fe, Co and Zn, Ni and V in APM and human tissues and body fluids
CZR	Cr in APM, U-Cr and S-Cr
IND	Cd, Ce and natural radionuclides in APM and human body fluids
INS	Cr, Zn, Mo and other enriched elements APM and human tissues and body fluids
KEN	Pb, Hg and Zn in APM and human tissues and body fluids
POR	Evaluation of health effects after determination of heavy elements in APM and human tissues
RUS	Pb, Cd, Cr, Zn, V, As, Sb, Se, Th and U in APM and human tissues
SAF	Determination of natural radioactivity in APM
SLO	Several elements in APM

5.5 Quality Assurance (QA)

The participants have the following protocols in place:

Country	Sampling Strategy	Sampling procedures	Sample preparation	Sample analysis	Available for APM / Biol.
BRA	Yes	Yes	Yes	Yes	Both
CPR	Yes	Yes	Yes	Yes	Both
CZR	(Yes)	Yes	Yes	Yes	Both
IND	Yes	Yes	Yes	Yes	Both
INS	Yes	Yes	Yes	Yes*	Both
KEN	Yes	Yes	Yes	Yes	APM
POR	(Yes)	Yes	Yes	Yes	Both
RUS	Yes	Yes	Yes	Yes	Both
SAF	Yes	Yes	Yes	Yes	APM
SLO	Yes	Yes	Yes	Yes	Both

() Data in brackets indicate protocols in preparation.

* In preparation for biological matrices.

Additional information on sampling will be provided to the participants through Denmark. Where possible, a typical QC protocol for the programme anticipated in the second phase of the CRP should already be implemented and reported in the progress report.

It was concluded that all the participants have some QA system based on the use of reference materials (RMs) and applied for in-house use.

For QA on sampling it is recommended to implement the following procedures:

- Check on samples analysed in duplicate
- Check on analyses of split samples
- Check on the influence of storage time
- Check on the influence of blanks
- Check on equipment performance and calibration
- Obtain adequate sample quantity to allow for re-analysis when required

The following procedures for the QA of analysis are recommended:

- Use inter- and intra laboratory comparisons. Where possible apply different analytical techniques to analyse for the same components.
- Several matrices should be used by all participants to evaluate their analytical performance. Possible matrices identified are:

For trace elements in APM:

Validation of INAA	NIST SRM 1648
Validation of PIXE, XRF	BCR CRM 128
Proficiency testing	IAEA filters (1-2), 3 Levels filters required

For trace elements in hair material:

Validation of INAA, PIXE, XRF	IAEA-087, GBW 09101, NIES CRM No. 13
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For analysis of As, Cd, Cr, Zn (Mn, Ni, Pb) in urine:

Validation of RNAA, PIXE?, XRF?	GBW 09103
Proficiency testing	Urine samples at 3 levels supplied by Denmark

For trace elements in blood:

Validation of RNAA, PIXE, XRF	Versieck's 2nd Generation RM (Human Serum), if still available
Proficiency testing	IAEA A -13

Action requested: The Agency will obtain information of the availability of suitable RMs for APM, blood, hair and nails. This will be the basis for final decision on RMs to be used by all participants.

Data evaluation on all data obtained in quality control exercises should be centrally compiled and evaluated.

Action requested: The Agency will investigate the possibility to offer this service.

The participants were informed that the ISO software for internal analytical quality control exists.

Action requested: The Agency will obtain information on the software, and if possible purchase and distribute it to all the participants.

6 ORGANIZATIONAL ASPECTS

6.1 Funding

The participants indicated to have found additional funding for their research programmes to support and strengthen their work within the CRP. Portugal indicated to have found only limited funding, while South Africa tries to liaise with industry and as such does not require additional funds.

6.2 Co-operation with others

The participants agreed to pay as much attention as possible to co-operation at the national and international level. The individual CRPs require as least the input from a local medical practitioner and international recognition of the CRP by the local WHO office on occupational health should be encouraged.

Action requested: The Agency will provide information on the local WHO offices to all participants.

An e-mail list-server for providing information to all participants simultaneously will be provided through Portugal.

6.3 Publications policy

The Agency strongly encourages and supports the publication of scientific data arising out of these studies. All CRP participants are therefore strongly recommended to use whatever means may be available to them to publish their data as soon as possible, preferably in a reputable peer-reviewed international scientific journal.

This recommendation refers specifically to publications describing the work carried out by individual CRP participants. The only constraints are that the Agency's support of this work should be acknowledged, and that a copy of the submitted manuscript should be sent to the Agency's project officer for information and comments.

A different policy applies to publications describing the results of projects that have been evaluated centrally. The preparation of such publications will, in the first place, be the responsibility of the Agency's technical officer. Such publications will be co-authored by *all* CRP participants who have contributed in any meaningful way to the outcome of the study.

6.4 Next Meeting

Another RCM for this CRP is expected to take place during the first half of 1999. It will provide the next opportunity for a group discussion of progress achieved under the CRP and of ways in which to co-ordinate the work for the remaining duration of the CRP.

The following possibilities will be explored for the next meeting to be held early in 1999, subject to approval by the host government:

Portugal and Brazil also mentioned their willingness to host the second meeting of the CRP. This can be organised anytime during the year.

7 RECOMMENDATIONS BY THE PARTICIPANTS

A number of recommendations by the participants are made in the foregoing sections of this report. The following priorities were agreed upon.

1. Standard reference materials and blanks should be provided by the Agency and incorporated in the quality assurance programme of the participants. If the sample quantity is the limitation at least one of the techniques should be chosen.
2. The Agency should explore the possibility of purchasing and distributing samplers with 2.5 μm AMAD cut-off particle size and appropriate pumps to all participants. The estimated costs per unit (samplers & pump) is about US\$ 1000.
3. The Agency should purchase and distribute to each participant the following software required for the project implementation: (1) a package for integrated method evaluation, internal quality control and proficiency testing, and (2) the IFCC-recommended statistical treatment of reference values.
4. It is recommended to incorporate the "Gent"-samplers in the sampling programme of the individual participating countries. It should be used at least to compare results with the ones using the existing sampling protocols.

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List of Participants

Dr. Maria Angela de B.C. Menezes
 Supervisao de Reator e Radioanalise
 Centro de Desenvolvimento da Tecnologia Nucl.
 Comissao Nacional de Energia Nuclear
 Rua Prof. Mario Werneck, s/n
 Caixa Postal 941, CEP 30123-970
 Belo Horizonte, Minas Gerais
 Brazil
 Fax: 00550314433908 or 4993380
 Tel: 00550314993253
 E-mail: menezes@urano.cdtb.br

Dr. Chifang Chai
 Department of Nuclear Analysis
 Institute of High Energy Physics
 Academia Sinica
 P.O. Box 2732, Beijing 100080
 China
 Fax: 00861062573660 (new), 00861068213374
 Tel: 00861062563339 ext. 4205 or
 00861064878438 (direct)
 E-mail: chaizf@lnat.ihepa.ac.cn

Dr. Xiaolin Hou
 Department of Nuclear Analysis
 Institute of High Energy Physics
 Academia Sinica
 P.O. Box 2732, Beijing 100080
 China
 Fax: 00861062573660
 E-mail: houxl@lnat.ihepa.ac.cn

Dr. Jan Kucera
 Nuclear Spectroscopy Department
 Nuclear Physics Institute
 Academy of Sciences of the Czech Republic
 CZ - 25068 Rez near Prague
 Czech Republic
 Fax: 0042026857003
 Tel: 00420266172268
 E-mail: kucera@ujf.cas.cz

Dr. J.M. Christensen
 National Institute of Occupational Health
 Lerso Parkhalle 105
 DK-2100 Copenhagen
 Denmark
 Fax: 004539165201
 Tel: 004539165252
 E-mail: jmc@ami.dk

Dr. Paul Alunkal Chacko (A.C. Paul)
 Environmental Radiological Laboratory
 Indian Rare Earths Limited
 Udyogamandal 683 501
 Kerala State
 India
 Fax: 0091484532469
 Tel: 0091484541061

Dr. H. Djojsubroto
 National Atomic Energy Agency
 Nuclear Technique Research Centre
 Jalan Tamansari No. 71
 Bandung 40132
 Indonesia
 Fax: 0062222504081
 Tel: 0062222503997
 E-mail: HELIA@IBM.MET

Dr. A. M. Kinyua
 Institute for Nuclear Science
 College of Engineering
 University of Nairobi
 P.O. Box 30197, Nairobi
 Kenya
 Fax: 002542336885 or 214912
 Tel: 002542334244 Exts. 28483/28536 or
 002542214912
 E-mail: antony.kinyua@lion.meteo.go.ke

Dr. Ma. Teresa Pinheiro
 Physics Department
 Nuclear and Technological Institute
 Estrada Nacional 10
 P-2685 Sacavem
 Portugal
 Fax: 0035119941525
 Tel: 0035119550021/1109
 E-mail: murmur@int1.itn.pt

Dr. M. V. Frontasyeva
 Dept. of Activation Analysis and Radiation
 Research,
 Frank Laboratory of Neutron Physics
 Joint Institute for Nuclear Research
 141980 Dubna, Moscow Region
 Russian Federation
 Fax: 0070962165085
 Tel: 0070959243914 or 0070962163653 (direct)
 E-mail: marina@nf.jinr.ru

Dr. Radojko Jacimovic
Laboratory for Radiochemistry
Department of Environmental Sciences
Institut Jozef Stefan
Jamova 39 - SI-1111 Ljubljana
Slovenia
Fax: 00386611612335
Tel: 00386611885-353
E-mail: radojko.jacimovic@ijs.si

Dr. A. Faanhof
Atomic Energy Corporation of South Africa Limited
P.O. Box 582
Pretoria 0001
South Africa
Fax: 0027123165944
Tel: 0027123166206 or Telefax: 0027126681947
E-mail: AFAANHOF@AEC.CO.ZA

Scientific Secretary:

Dr. Borut Smodis
Section of Nutritional and Health-Related
Environmental Studies
Department of Human Health
IAEA
P.O. Box 100
A-1400 Vienna
Austria
Fax: 43-1-26007
Tel: 43-1-2600-21652
B.Smodis@IAEA.ORG

**FIRST RESEARCH CO-ORDINATION MEETING (RCM) FOR THE CO-ORDINATED
RESEARCH PROJECT (CRP) ON ASSESSMENT OF LEVELS AND HEALTH-EFFECTS
OF AIRBORNE PARTICULATE MATTER IN MINING, METAL REFINING AND METAL
WORKING INDUSTRIES USING NUCLEAR AND RELATED ANALYTICAL TECHNIQUES**

AGENDA

MONDAY, 20 OCTOBER 1997

9:45 - 10:00 Registration

10:00 - 12:00 SESSION 1: *Chair: M.Â. Menezes*

Opening
Introduction of the participants
Administrative arrangements for the meeting
Adoption of the agenda
Status report on the Co-ordinated Research Project

PROJECT REPORTS (Presentation of working papers)

Brazil The first metal evaluation using nuclear and related
analytical techniques in state of Minas Gerais - Brazil
M. Â. Menezes

12:00 - 14:00 LUNCHEON

14:00 - 17:00 SESSION 2: *Chair: C. Chai*

PROJECT REPORTS (continuation)

China A study on environmental pollution monitoring and
occupational health in the Capital Iron and Steel
Company, Beijing, China, using nuclear and related
analytical techniques
C. Chai

Czech Republic Biological monitoring of exposure to selected toxic
metals in electroplating workers using NAA and PIXE
techniques
J. Kučera

India Characterization of airborne Ce, Th and Cd in
workplace and their co-relation with their
concentrations in body fluids and excreta of
occupational workers using NAA, ICP-AES and XRF
P. Alunkal

17:00 Reception

TUESDAY, 21 OCTOBER 1997

09:00 - 12:00 SESSION 3: *Chair: J. Kučera*

PROJECT REPORTS (continuation)

- | | |
|-----------|---|
| Indonesia | The use of nuclear and related techniques for the studies of airborne particulate matter in workplace including tissue analysis and possible impact on human health in a metal industry
<i>H. Djojotubroto</i> |
| Kenya | Workplace monitoring and occupational health studies in Kenya using nuclear and related analytical techniques
<i>A. M. Kinyua</i> |
| Portugal | Particulate matter and health - from air to human lung
<i>M. T. Pinheiro</i> |

12:00 - 14:00 LUNCHEON

14:00 - 17:00 SESSION 4: *Chair: P. Alunkal*

PROJECT REPORTS (continuation)

- | | |
|--------------------|--|
| Russian Federation | Workplace monitoring and occupational health studies at the Centre for Production of Phosphorus Mineral Fertilizers, Voskresensk (Moscow Region, Russia), using nuclear and related analytical techniques
<i>M. Frontasyeva</i> |
| Slovenia | Workplace monitoring and occupational health studies in the Šoštanj Thermal Power Plant, Slovenia
<i>R. Jačmović</i> |
| South Africa | Workplace monitoring and related health hazard evaluation in South African mining and mineral processing industries by application of nuclear and related analytical techniques
<i>A. Faanhof</i> |

WEDNESDAY, 22 OCTOBER 1997

- 09:00 - 12:00** **SESSION 5:** *Chair: H. Djojosebroto*
- 09:00 - 11:30** **SEMINARS**
(See separate list)
- 11:30 - 12:00** **GENERAL DISCUSSION**
(See separate list of discussion topics)
- 12:00 - 14:00** **LUNCHEON**
- 14:00 - 17:00** **SESSION 6:** *Chair: J. M. Christensen*
GENERAL DISCUSSION (continuation)

THURSDAY, 23 OCTOBER 1997

- 09:00 - 12:00** **SESSION 7:** *Chairs: A. M. Kinyua / M. T. Pinheiro*
GENERAL DISCUSSION (continuation)
- 12:00 - 14:00** **LUNCHEON**
- 14:00 - 17:00** **SESSION 8:** *Chairs: M. Frontasyeva / R. Jaćmović*
GENERAL DISCUSSION (continuation)

FRIDAY, 24 OCTOBER 1997

- 09:00 - 12:00** **SESSION 9:** *Chair: A. Faanhof*
FINAL DISCUSSIONS
Report of the meeting
CLOSING OF THE MEETING
- 12:00-open end** Personal discussions

LIST OF SEMINAR TOPICS

1. J. M. Christensen: Biological monitoring of toxic metals: factors influencing interpretation of biomonitoring results
2. J. M. Christensen: New developments in biological monitoring of inorganic chemicals
3. M. V. Frontasyeva: A brief sketch of data obtained in early 1990' for the complex workplace monitoring and occupational health studies at the metallurgical plant in Belovo (Kemerovo Region, Eastern Siberia, Russia), reprocessing zinc ores
4. J. Kučera: TRACY - An international project for obtaining reference values for concentrations of trace elements in human blood and urine
5. B. Smodiš: Recent IAEA projects on air pollution

**FIRST RESEARCH CO-ORDINATION MEETING (RCM) FOR THE CO-ORDINATED
RESEARCH PROJECT (CRP) ON ASSESSMENT OF LEVELS AND HEALTH-EFFECTS
OF AIRBORNE PARTICULATE MATTER IN MINING, METAL REFINING AND METAL
WORKING INDUSTRIES USING NUCLEAR AND RELATED ANALYTICAL TECHNIQUES**

LIST OF DISCUSSION TOPICS

PURPOSE AND SCOPE OF THE CRP

1. Summaries of the presentations of individual projects

- 1.1 Scientific background
- 1.2 Scientific scope
- 1.3 First year programme of work
- 1.4 Output of the first year

2. Identified areas of a research plan

- 2.1 The Core Programme
 - 2.1.1 Definition of the core programme
 - 2.1.2 What are the priorities among the topics?
 - 2.1.3 Are there any other topics that should be included?
- 2.2 The Supplementary Programme
 - 2.2.1 What topics are to be included in the supplementary programme?
 - 2.2.2 What are the priorities among the various topics that have been suggested?

3. Expected benefits of this research

- 3.1 For the participating countries
- 3.2 For science in general

4. Updating of individual projects

- 4.1 Approach
- 4.2 Programme of work for the second year
- 4.3 Expected output/results for the second year

TECHNICAL ASPECTS

5. Selection of sampling sites and types of samples to be collected

- 5.1 What are the criteria for the selection of sampling sites?
- 5.2 How many sampling sites are needed for each project?
- 5.3 What kinds of samples should be collected?
- 5.4 How many samples should be collected and over what sampling periods?

6. Sampling techniques and equipment

- 6.1 What kinds of sampling techniques and sampling devices are recommended (for air particulate matter, for biological material)?
- 6.2 How can the samples obtained by different kinds of samplers be related to each other?
- 6.3 Should any kind of sampling device be provided centrally, by the Agency?

7. Analysis

- 7.1 Is advice needed on any of the analytical techniques that are being used in the CRP?
 - 7.1.1 For nuclear-related analysis (NAA, XRF, PIXE, ICP-MS)?
 - 7.1.2 For analysis by other techniques (ICP-OES, AAS, techniques for organic components, etc.)?
 - 7.1.3 For sample preparation prior to analysis (e.g. use of clean working areas)?
- 7.2 Is any additional advice needed on the selection and prioritization of analytes to be determined in connection with health effects for specific sources of pollution?
- 7.3 Is there a need to identify "reference analytical laboratories" for any particular analytes and/or techniques, and, if so, what is the function of these reference laboratories, e.g.
 - 7.3.1 As sources of specialized advice;
 - 7.3.2 To assist collection centres that otherwise do not have sufficient analytical capacity (i.e. in order to be able to analyze more samples, or to determine more analytes);
 - 7.3.3 For cross-checking of some of the analytes

8. Data processing and interpretation

- 8.1 Database management, e.g. should this be done with any specific kind of software?
- 8.2 Data evaluation and presentation: What types of software are being used/which are recommended?
- 8.3 Central data processing, is there a need to appoint a central data co-ordinator:

9. Quality Assurance

- 9.1 How many of the participants have written protocols:
 - 9.1.1 For sampling procedures?
 - 9.1.2 For sample preparation procedures?
 - 9.1.3 For sample analysis procedures?
- 9.2 Have participants adopted any quality assurance procedures for "in-house" use?
- 9.3 Quality assurance of sampling: what procedures are recommended for each type of sample?
- 9.4 Quality assurance of analysis: what procedures are recommended:
 - 9.4.1 For "in-house" use?
 - 9.4.2 As an external quality control scheme?
- 9.5 Quality assurance of data reporting and evaluation: what procedures are recommended?

ORGANIZATIONAL ASPECTS

10. Funding

- 10.1 Have participants found additional sources of funding their research programmes?

11. Co-operation with others; suggestions for making and improving co-operation with others

- 11.1 In this CRP (between participants)
- 11.2 Nationally
- 11.3 Internationally (e.g. UNEP, WHO, etc.)

12. Role of the Agency's Laboratory, Seibersdorf; what role is suggested for:

- 12.1 Methods development and validation?
- 12.2 Quality assurance services?
- 12.3 Backup and service analyses?

13. Technical co-operation projects and training: are there any suggestions for future activities?

14. Information exchange within the CRP - how can this be best promoted?

15. Expert meetings and publications: are there any suggestion for future activities?

16. Publications policy for work done within the framework of the CRP: do we need a publications policy and, if so, what should it be?

17. The next RCM: where and when should this be?

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**Information on Individual Participant's Work
for the First Year and Plans for the Second Year**

Contributions are arranged according to the countries' names

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TITLE: The first metal evaluation using nuclear and analytical techniques in State of Minas Gerais - Brazil

CSI: Maria Angela de B.C. Menezes

INSTITUTE: Supervisao de Reator e Radioanalise
Centro de Desenvolvimento da Tecnologia Nucl.
Comissao Nacional de Energia Nuclear
Rua Prof. Mario Werneck, s/n
Caixa Postal 941, CEP 30123-970
Belo Horizonte, Minas Gerais
BRAZIL

SCIENTIFIC BACKGROUND:

The industrial process introduce the contamination risks to the workers all the time. Belo Horizonte and its neighborhood are the second industrial center of Brazil, but there are not registers about the level of metal concentration in the environmental area in the industry, nor even of the level of worker's contamination.

SCIENTIFIC SCOPE:

Biological monitors of exposure assess the health risk through the evaluation of the level of incorporation or exposure. Using the biomonitor filters, there will be a survey of the exposures to metal related to occupational diseases in galvanizing industry, which is responsible for the majority of occurrences of occupational diseases.

PROGRAMME OF WORK FOR THE FIRST YEAR:

1. Choice of the critical metals and specific industry
2. Arrangements with industry
3. Sampling methodology
4. Sampling hair, nails, blood, personal filters from control group
5. Chemical analysis of samples - preliminary tests

OUTPUT FOR THE FIRST YEAR:

Concerning to the work plan:

1. It was decided to study the galvanizing industry
2. The first contact was made with many of them
3. The methodology of sampling has been established
4. It was decided to postpone the step of sampling biomonitor filters of the control group, because it was decided to collect from studying group, in order to identify the metals.
5. It was sampled biomonitor filters from studying group and the preliminary results were obtained by Ko neutron activation analyses.

APPROACH FOR THE SECOND YEAR:

In this 2nd year, the collecting will go on as well the application of Ko neutron activation analysis. The technique of atomic absorption will be applied too.

PROGRAMME OF WORK FOR THE SECOND YEAR:

1. Statistical studies (number of workers, of industries, frequency of collecting)
2. Sampling hair, blood, nails, personal air filters from workers
3. Sampling hair, blood, nails, personal filters from control group
4. Chemical and radio analytical analysis
5. Analysis of the results/choose of metal (s).

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

To have enough results to decide if it will be necessary to collect more samples or not; if the results are enough to make correlations with some occupational diseases.

TITLE: A Study on environmental pollution monitoring and occupational health in the Capital Iron and Steel Company, Beijing, China, using nuclear and related analytical techniques

CSI: Chifang Chai

INSTITUTE: Department of Nuclear Analysis
Institute of High Energy Physics
Academia Sinica
P.O. Box 2732, Beijing 100080
CHINA

SCIENTIFIC BACKGROUND:

The atmospheric pollution in China is becoming more and more serious with the economic growth in the past decades. The airborne particle concentration in Beijing far exceeds the allowable level set by the Chinese Government, mainly from the Capital Iron and Steel Company (CISC).

SCIENTIFIC SCOPE:

In the framework of the CRP, the intended project bears on the environmental monitoring at the CISC and on its effects to occupational health of the workers exposed to the workplace.

PROGRAMME OF WORK FOR THE FIRST YEAR:

The polluted workplace, its surrounding region and one control area are defined, the suitable analytical techniques for some target elements in environmental and biological samples are validated.

OUTPUT FOR THE FIRST YEAR:

An agreement with the CISC for 4 year cooperation project was signed. The human hair, blood and urine samples of 50 furnace men, 50 rear-service and administrative staff members and some people living at the surrounding and the control regions have been collected and prepared for analysis. All hair samples were analyzed by INAA, which has been validated.

APPROACH FOR THE SECOND YEAR:

The nuclear (INAA, PIXE, SRXRF) and non-nuclear (ICP-MS) will be applied for analysis of the target elements in the environmental and biological samples.

PROGRAMME OF WORK FOR THE SECOND YEAR:

- 1) Collection and preparation of all environmental (air-borne particle, soil, water and plant) and all human samples (hair, blood and urine).
- 2) Optimization of nuclear analysis techniques.
- 3) Analysis and data processing.

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

The sampling will be completed and part of samples will be analyzed. Three evaluation methods (in-house working material, reference material and inter-laboratory comparison) will be used for analytical quality assurance.

TITLE: A Monitoring of exposure to selected toxic metals in workers of a ferroalloy production plant using NAA and PIXE

CSI: Vladimir Hnatowicz

INSTITUTE: Nuclear Physics Institute (NPI)
of Academy of Sciences of the Czech Republic
CZ-250 68 Rez near Prague
CZECH REPUBLIC

SCIENTIFIC BACKGROUND:

- i) Determination of Cr, Mn and other metals in air particulate matter born in the workplace air and collected by personal samplers (PM 2.5, PM 10) by INAA and PIXE.
- ii) Determination of Cr (Mn) in serum, erythrocytes, urine, hair and nails of occupationally exposed and control persons.
- iii) Examination of correlations between the parameters investigated.

PROGRAMME OF WORK FOR THE FIRST YEAR:

- i) Validation of INAA and PIXE techniques for determination of Cr and Mn in air particulate matter (APM).
- ii) Validation of sampling procedures, especially for samples prone to contamination, such as blood.
- iii) Procurement of sampling devices, a transportable air filtration unit providing Class 10 clean environment for sampling and sample handling of biological samples, high purity quartz vials for NAA (Heraeus Suprasil AN), etc.

OUTPUT OF THE FIRST YEAR:

- i) The accuracy of our INAA procedures for the determination of Cr and Mn in APM samples has been proved by analysis of NIST SRM 1648 and for determination of Mn by analysis of NIST SRMs 1633a, 2704 and BCR CRMs 038, 101, 143.
- ii) INAA procedures for low level determination of Cr and Mn in biological materials were developed and their validation is in progress.
- iii) Severe contamination problems were detected on using SARSTEDT and BECTON DICKINSON devices for blood sampling which are recommended by the producers for "trace (metal) element analysis".

APPROACH FOR THE SECOND YEAR:

- i) Completing of validation of sampling and analytical procedures
- ii) Sampling of APM and of human tissues from workers of the ferroalloy production plant.

PROGRAMME OF WORK FOR THE SECOND YEAR:

- i) Determination of Cr (Mn) in reconstituted and freeze-dried Versieck's human serum, 2nd generation reference material to demonstrate both validity of the sampling procedure for blood collection and the accuracy of analytical results, respectively.
- ii) Collection of APM born in the workplace air by personal samplers and determination of Cr (Mn) and other metals in the samples by INAA and PIXE.
- iii) Collection of blood, urine, hair and nails from the exposed workers and analysis of the samples for their Cr (Mn) content by RNAA and INAA.

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

Analysis results of the above-mentioned samples and examination of correlations of the parameters studied.

TITLE: Characterization of airborne Ce, Th and Cd in workplace and their correlation with their concentrations in body fluids and excreta of occupational workers using NAA, ICP-AES and XRF

CSI: Alunkal Chacko Paul

INSTITUTE: Bhabha Atomic Research Centre, Health Physics Division
Environmental Radiological Laboratory
Indian Rare Earths Limited
Udyogamandal 683 501
Kerala State
INDIA

SCIENTIFIC BACKGROUND:

Airborne particulates constitute one of the major routes of occupational exposure in environmental mineral processing industries affecting the health of the worker. Assay and characterization of the critical pollutants in the work atmosphere assume significance in the context of occupational health protection. There is need to establish reliable analytical techniques to monitor the exposures in order to offer scientific solutions for protection in work place.

SCIENTIFIC SCOPE:

The work aims at characterization of airborne particulate matter in the work atmosphere with respect to particle size, solubility class and chemical species in order to obtain realistic information on uptake. The information is to be validated by biological monitoring of body fluids and excrete of occupational workers. Since the assay involves very low levels, nuclear and related analytical techniques of high sensitivity are employed in the studies.

PROGRAMME OF WORK FOR THE FIRST YEAR:

The programme consisted of the following preliminary investigations:

1. Physical characterization of airborne particles in the work place such as the particle sizing involving determination Mass Median Aerodynamic Diameter (MMAD) and Activity Median Aerodynamic Diameter (AMAD) for Th, Ce and Cd.
2. Experiments to simulate the biochemical solubility of the particulate matter in the lung, and
3. Determination of Th and Ce in the urine secretion of occupational workers.

OUTPUT FOR THE FIRST YEAR:

MMAD for airborne particulate were obtained at the monazite mineral plant and zinc smelter plant. The MMAD and AMAD at the monoxide & mineral plant ranges from 3 to 10 μm . The MMAD at the zinc smelter plant showed large variations attributed to the nature of the process. MMAD of 3 μm was observed at the Cd electro plating process. The urine sample of

workers at the monazite mineral plant showed mean values of 182 ng l⁻¹ and 700 ng l⁻¹ for Th and Ce respectively. The ratio of Ce to Th in the urine samples nearly reflected the ambient mass concentration ratios of these elements.

APPROACH FOR THE SECOND YEAR:

The studies are to be extended to cover more occupational areas for representative particle sizing. Solubility class of the airborne particulate are to be obtained through detailed experiments. Biological monitoring has to be more broad based to cover statistically significant number of samples and obtain reliable correlations between different body components. Environmental site specific background has to be evolved for different study areas, especially the high background natural radiation areas.

PROGRAMME OF WORK FOR THE SECOND YEAR:

1. Detailed elemental (Th, Ce and Cd) characterization of the airborne particulate.
2. Biochemical mobilization studies employing simulated lung serums and digestive fluid.
3. Correlation of the airborne levels with blood, urine and breath (as applicable).
4. Establishment of site specific background levels.

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

Information of particle sizing to be completed and the results firmed up. Biochemical leaching data to be obtained to correlate the excretion and retention in the body. Relation between ambient air quality and biological samples is expected to be clearer.

TITLE: The use of nuclear and related techniques for the studies of airborne particulate matters in workplace including tissue analysis impact on human health in a metal industry

CSI: Benjamin Widjajakusuma

INSTITUTE: National Atomic Energy Agency
Center for Nuclear Technique Research
Jalan Tamansari
Bandung 40132
INDONESIA

SCIENTIFIC BACKGROUND:

Various processes in a metal industry may produce fine dust particulate that are hazardous to human health. Elements in the dust particulate may enter human body through respiration and direct contact through skin.

SCIENTIFIC SCOPE:

In this work elemental levels such as Cu, Cr, Mo, Zn will be determined in airborne particulate matter (collected from workplace), blood, hair and nail of industrial workers.

FIRST YEAR PROGRAMME OF WORK:

To identify the health symptoms of the workers that are subjected to medical examinations (medical history, physical examinations and routine blood check), and neutron activation analysis of elements in airborne particulate samples, blood, hair and nails of the workers.

OUTPUT FOR THE FIRST YEAR:

Data on health conditions of the workers, elemental levels in blood, hair and nails of the workers.

APPROACH FOR THE SECOND YEAR:

Determination of elemental levels in blood, hair and nails of the workers, especially for elements of high enrichment factor in airborne particulate samples and suspected elements from medical examinations. The levels of these elements in blood, hair and nail of the workers will be compared to those of normal individuals.

PROGRAMME OF WORK FOR THE SECOND YEAR:

Collecting blood, hair and nail samples from health individuals (control) and determination of elemental levels in these samples. The same study of workers in aluminum industry will be carried out.

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

Comparative data on levels of elements in blood, hair and nail samples of industrial (metal and aluminium) workers and those of control and their correlation with the observed health symptoms.

TITLE: Heavy Metal Analysis of Suspended Particulate Matter (SPM) and other Samples from some Workplaces in Kenya

CSI: Antony M. Kinyua

INSTITUTE: Institute for Nuclear Science
Faculty of Engineering
University of Nairobi
P.O. Box 30197, Nairobi
KENYA

SCIENTIFIC BACKGROUND:

Cases of occupational asthma, byssinosis, silicosis and asbestosis have been reported in various industrial workers (battery manufacturing, cement production and mineral processing) in Nairobi, Athi River, Thika and Mombasa. Recent studies have shown that occupational diseases are becoming a growing problem in Kenya. This is due to the rapid rate of industrialization coupled with ignorance of the dangers caused by lack of cleaner production practices by some of the local industries.

SCIENTIFIC SCOPE:

In this work, elemental levels of Zn, Pb, Fe, Ca, Mn, Ni, Cu and Hg will be determined by EDXRF, TXRF, AAS and PIXE from the particulate samples collected from various workplaces by PM-10 system. Other samples from industrial effluents and products will be analysed for heavy metals by use of the above techniques. It is therefore the aim of this study to continue enhancing the use of NRAT's in workplace monitoring and occupational health studies to begin providing assessment data for future epidemiological cases studies.

PROGRAMME OF WORK FOR THE FIRST YEAR:

- a) Continuation of particulate matter sampling in various industries and workplaces through the PM-10 technique using the "Gent Sampler".
- b) Commencement of particulate matter sampling at Mt. Kenya (14,500 ft.) using the streaker sampler.
- c) Continue holding meeting/seminars with the management and relevant government authorities on the accrued results.
- d) Initiation of monitoring of chemical exposures - CO, HC, NO_x, SO₂ and NH₃.

OUTPUT OF THE FIRST YEAR:

- 1) Publication of results in a scientific journal
- 2) Submission of progress report and contract renewal documents
- 3) Holding a seminar with the authorities and industry on cleaner production practices
- 4) Expertise in particulate matter sampling, data analysis and dissemination of the accrued information.
- 5) Literature/Data on health problems of industrial workers.

APPROACH FOR THE SECOND YEAR:

- 1) Continuation of workplace monitoring and sample collection
- 2) Determination of heavy metals in the particulate samples collected from workplaces and the Mt. Kenya sampling site
- 3) Initiation of epidemiological case studies
- 4) Initiation of risk assessment studies on the occupational health problems.

PROGRAMME OF WORK FOR THE SECOND YEAR:

- 1) Continue heavy metal determination of suspended particulate matter collected from workplaces and Mt. Kenya
- 2) Initiate epidemiological case studies to investigate association between long-term exposure to particulate matter (and other air pollutants) and adverse health effects, including time of life lost, chronic illness, and conditions that increase susceptibility of air pollutants.
- 3) Holding of seminars/workshops with industry and authorities.

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

- 1) Publication of results in a scientific journal and presentation in seminars and local workshops,
- 2) Progress report and contract renewal documents
- 3) Expertise in epidemiological case studies
- 4) Data of relative public burdens of long-term and short-term exposure of ambient suspended particulate matter (SPM).

TITLE: Particulate matter and health - from air to human lung

CSI: Maria Teresa Pinheiro

INSTITUTE: Physics Department
Nuclear and Technological Institute
Estrada Nacional 10
P-2685 Sacavem,
PORTUGAL

SCIENTIFIC BACKGROUND:

Evidences were gathered on the effects of air pollutants in human health. The adverse respiratory effects have been related to airborne particulate matter.

SCIENTIFIC SCOPE:

The aim of this project is to search for respiratory system particular aggressors to which workers are submitted in their labouring activities that may influence their health.

FIRST YEAR PROGRAMME OF WORK:

The work comprised a prospective study on workers respiratory health status survey and workplace indoor air monitoring in order to assess risks to human health.

OUTPUT FOR THE FIRST YEAR:

32 workers from steel process and casting sector of a steel plant have been examined for blood elemental content and for their lung function evaluation. The results point out that the number of years of exposure are related to the occurrence of respiratory affections (18% of the cases).

If the K, Ca, Fe, Cu, Zn, Se blood content, as well as respiratory complaints, smoking habits, years of exposure are used as an input matrix for cluster analysis, the cases with positive respiratory complains agglomerate. This separation is more evident in serum, than in Packed Blood Cells fraction.

APPROACHES FOR THE SECOND YEAR:

Occupational health studies often need periodical examination both from the environmental parameters and from the individuals so exposed. Therefore, during the second year of project the main actions set in the work plan will be repeated.

PROGRAMME OF WORK FOR THE SECOND YEAR:

- 1) Continuation of workplace air monitoring.
- 2) Second year medical examination of workers previously observed and measurement of health status parameter.
- 3) Air particulate matter assessment in the respiratory ducts, lung tissue and excretion organs.

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

To assess risks to human respiratory health from information gathered from workplace airborne particulate matter composition health affections occurrence and elemental association in the respiratory system similar to those found in air particulate matter.

TITLE: Workplace monitoring and occupational health studies at the Centre for production of phosphorus mineral fertilizers, Voskresensk (Moscow Region, Russia), using nuclear and related analytical techniques.

CSI: Marina Frontasyeva

INSTITUTE: Dept. of Activation Analysis and
Radiation Research
Frank Laboratory of Neutron Physics
Joint Institute of Nuclear Research
141980 Dubna, Moscow Region
RUSSIAN FEDERATION

SCIENTIFIC BACKGROUND:

The production of phosphorus fertilizers has a pathological impact on its occupational staff. Nuclear and related analytical techniques enable relationships to be established between concentrations of element pollutants (Cr, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, rare-earth elements (REE) Th, U, and others) in raw material (apatite concentrate), byproduct (Phosphogypsum), humans (biosubstrates: hair, nails, teeth), and the workplace. This allows to determine how man's biosubstrates can be used to follow the rate of pathological changes in the organism as it is being exposed to intense technogenic environments.

SCIENTIFIC SCOPE:

During 1989-1993 the plant was rebuilt so that it could more efficiently utilize phosphogypsum, the main waste product from the production. To clarify the present situation, it is necessary to:

- determine the content and level of air pollution in the working area and drinking water;
- determine the normal and abnormal concentrations of elements in biosubstrates (hair, nails, bone tissue-teeth) of the occupational staff. The presence in significant amounts of REE in biosubstrates shows that they participate in biological cycles of growth. Using epithermal NAA, (with radiochemical separation when necessary) the character of the REE's distribution in human biosubstrates is to be studied.

PROGRAMME OF WORK FOR THE FIRST YEAR:

Month 1-4

- sampling air, industrial dust, drinking water, raw material (apatite concentrate) and byproduct (phosphogypsum)
- multi element analysis of environmental samples by epithermal NAA in Dubna and XRF in the Institute of Geology, Moscow.

Month 5-6

- sampling of biosubstrates (hair, nails, bone tissue-teeth) of occupational staff according to the methods of WHO.

Month 7-9

- multi element analysis of biosubstrate samples by epi-NAA in Dubna, and XRF in GIN RAS.

Month 9-12

- data processing
- preparation of an annual report.

OUTPUT FOR THE FIRST YEAR:

1. The main chemical pollutants at the plant are F, Ca, As, Sb, REE, Th and U, which is confirmed by the analysis of the atmospheric aerosols and the hair of the occupational staff. The main source of pollution is the raw material (apatite concentrate).
2. The drinking water consumed at the plant could not be considered as a source of the uptake of the above-mentioned elements into a human organism.
3. Due to atmochemical network the workplaces characterized by the increased level of trace element pollution in air are revealed.
4. The trace element content of hair of the occupational staff reflects the pollution of the workplaces.
5. More thorough study of trace elements in teeth could help to reveal the interrelation between the concentration of Ca, Fe, Sr, and REE.
6. One should note that the further sampling of dust is not reasonable.

APPROACH FOR THE SECOND YEAR:

For the logical completion of the present study, the following plan is suggested:

- To carry out an additional sampling of the atmospheric aerosols in the work places, as well as hair and teeth of the occupational staff, aimed at accumulating a reasonable amount of data for a reliable statistical interpretation of the results obtained.
- As fluorine is emitted in the production of phosphorus fertilizers causing *fluorosis* in the occupational health, we plan to determine the fluorine content in the air of the work places of the plant and in the hair of the occupational staff.
- Since there are data on the substitution of Ca by Sr in bones, it would be interesting to examine such distribution in teeth by means of XRF and NAA.
- The noted selective differentiation of REE in biosubstrates (preferable accumulation of Eu and Ce in teeth and hair) could be thoroughly studied using radiochemical NAA.

- Correlation of the biochemical data obtained with the resulting health effects should be examined.

PROGRAMME OF WORK FOR THE SECOND YEAR:

Month 1-3

- continuation and completion of NAA of hair, dust, industrial products, wastes, raw material.
- data processing.
- comparison with the previous data obtained during the first year of the project.

Month 4-6

- collection of aerosols and biosubstrates for fluorine content.

Month 7-9

- NAA of aerosols and biosubstrates followed by radiochemical separation.

Month 10-12

- statistical analysis of the results
- preparation of the annual report.

We plan to use the third year of the project (with a possible extension to 5 years) for repeating the workplace monitoring of the fertilizer plant and extending the study to the occupational staff and local residents of the phosphate ore open-cast mining enterprise, situated 3-7 km from the main plant.

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

Estimation of the sanitary-hygienic situation at the plant by comparing the elemental contamination of workplace and biosubstrates of occupational staff with the results of medical tests.

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TITLE: Workplace monitoring and occupational health studies in the Sostanj Thermal Power Plant, Slovenia

CSI: Radojko Jacimovic

INSTITUTE: Laboratory for Radiochemistry
Department of Environmental Sciences
Institute "Jozef Stefan"
Jamova 39
SL-1111 Ljubljana
SLOVENIA

SCIENTIFIC BACKGROUND:

Up to now, only a few investigations have been performed in the Sostanj Thermal Power Plant (TPP) involving comprehensive studies of trace elements, toxic elements, heavy metals and radio nuclides in the workplaces. The aim of the project is development and application of nuclear and nuclear-related analytical techniques for workplace pollution and occupational health studies leading to formation of a database concerning the trace element air pollution inside the Sostanj TPP.

SCIENTIFIC SCOPE:

The general scope of the project is a better knowledge of the state of air pollution in premises of Sostanj Thermal Power Plant by performing workplace monitoring and occupational health studies involving determination of trace element air pollution from industrial emissions by analyzing airborne particulate matter (APM) and biological samples taken from exposed workers.

PROGRAMME OF WORK FOR THE FIRST YEAR:

1. To determine critical groups of workers in the plant.
2. To choose sampling workplace sites.
3. To start sampling two fractions, separated by aerodynamic diameter into a fine fraction (0-2.5 μ m) and a coarse fraction (2.5-10 μ m).

OUTPUT FOR THE FIRST YEAR:

Validated nuclear and nuclear-related techniques for analyzing collected aerosol samples (Ko-INAA, EDXRF and TXRF).
Appropriate samplers for collecting APM will be chosen.

APPROACH FOR THE SECOND YEAR:

1. To determine the mass fractions of dust based on the gravimetric method.
2. To determine elemental concentrations with various analytical methods (EDXRF, TXRF, PIXE, Ko-INAA).
3. Sampling human biological samples based on medical advice.

PROGRAMME OF WORK FOR THE SECOND YEAR:

To continue systematic trace element air pollution monitoring and research in the workplaces of the Sostanj TPP using nuclear and nuclear-related techniques.

Airborne particulate matter and biological samples taken from occupationally exposed humans will be systematically analyzed.

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

- Elemental content in APM obtained by nuclear and related analytical techniques.
- Preliminary results for species of toxic elements in the dust (e.g. Cr^{3+} and Cr^{6+}).
- Concentrations of organic pollutants using various sampling methods and analytical techniques.

TITLE: Workplace monitoring and related health hazard evaluation in South African mining and mineral processing industries by application of nuclear and related analytical techniques

CSI: Arnaud Faanhof

INSTITUTE: Atomic Energy Corporation of South Africa Limited
P.O. Box 582
Pretoria 0001
SOUTH AFRICA

SCIENTIFIC BACKGROUND:

Southern Africa, being one of the major mineral producers in the world, has a vast number of workers being possibly exposed to a variety of elemental and natural radionuclide constituents. Although South African regulations are available, the real impact has still to be assessed for the workers and the general public. This is an ongoing process backed by legislation; thus providing results on a large variety of industries. This offers the opportunity to contribute to the CRP, the yearly results obtained on a number of mining and mineral processing industries.

SCIENTIFIC SCOPE:

To assess health related impacts of mining and mineral processing operations on the workers, the public and the environment.

Both natural radioactivity and inorganic elements are evaluated in airborne dust, surface and groundwater, soil and sediments and the human food chain.

PROGRAMME OF WORK FOR THE FIRST YEAR:

Evaluation of available information from surveys and routine analyses done for the Southern African mining and mineral processing industries over the last two years. Compilation of the data and presentation at the first meeting of the CRP.

OUTPUT FOR THE FIRST YEAR:

Compilation of available data on APM of Southern African mining and mineral processing industries. Evaluation of impact on workers, the public and the environment.

APPROACH FOR THE SECOND YEAR:

A number of mining and mineral processing industries have been approached to incorporate in their radiological survey of 97-98 the assessment of inorganic elemental impact on the workers. The elemental analysis will be done by INAA, while radioanalytical work by INAA and radiometric methods.

PROGRAMME OF WORK FOR THE SECOND YEAR:

Compile the available data from the 1997/98 routine services provided to the mining and mineral processing industries in Southern Africa.

EXPECTED OUTPUT/RESULTS FOR THE SECOND YEAR:

Presentation of relevant studies performed during the duration of the second year of the CRP.

Contract nº 9473/RO/ Regular Budget Fund



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**WORKPLACE AND OCCUPATIONAL HEALTH: THE FIRST METAL
EVALUATION USING NUCLEAR AND ANALYTICAL TECHNIQUES IN THE
STATE OF MINAS GERAIS - BRAZIL**

**Centro de Desenvolvimento da Tecnologia Nuclear (CDTN)
Comissão Nacional de Energia Nuclear (CNEN)**

Maria Ângela de Barros Correia Menezes

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CO-ORDINATED RESEARCH PROGRAMME
ASSESSMENT OF LEVELS AND HEALTH-EFFECTS OF AIRBORNE
PARTICULATE MATTER IN MINING, METAL REFINING AND METAL WORKING
INDUSTRIES USING NUCLEAR AND RELATED ANALYTICAL TECHNIQUES

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Maria Ângela de Barros Correia Menezes
CDTN/CNEN – Supervisão de Reator e Radioanálise – Setor de Radioquímica
Caixa Postal 941 – CEP 30123.970 – Belo Horizonte – Minas Gerais – Brazil
Fax: 55 031 4993380/4993444 e-mail: menezes@urano.cdtb.br

Silvânia Vaz de Melo Mattos
FUNED – Divisão de Bromatologia e Toxicologia – Serviço de Química Especializada
Av. Conde Pereira Carneiro, 8 – CEP 30550.010 – Belo Horizonte – MG – Brazil

Serafim Santos Filho
Secretaria Municipal de Saúde de Belo Horizonte, Coordenação de Saúde do Trabalhador
Av. Afonso Pena, 2336, 4º andar, Funcionários - CEP 30130.007 – Belo Horizonte – MG – Brazil

Eugênio Diniz
FUNDACENTRO/BH – Av. Afonso Pena, 726, 23º and. – CEP 30130.002 – Belo Horizonte – MG – Brazil

Claudia de Vilhena Schayer Sabino
CDTN/CNEN – Supervisão de Reator e Radioanálise – Setor de Radioquímica
Caixa Postal 941 – CEP 30123.970 – Belo Horizonte – Minas Gerais – Brazil
Fax: 55 031 4993380 e-mail: sabinoc@urano.cdtb.br

1. ABSTRACT

Belo Horizonte, the capital of the State of Minas Gerais and its neighbourhood are the second industrial center of Brazil, concentrating many industries in several areas mainly metal refining and transformation. There are no registers about the level of metal concentration in the environmental air in the industry, nor even of the level of workers' contamination. The overall objective of this Project is to make a survey of the exposures to metals related to occupational diseases in galvanizing industry, which is responsible for the majority of occurrences of occupational diseases. The survey will be accomplished using as bioindicators hair, nails, blood, urine, and individual air filters. These matrixes

will indicate the incorporation of metals and the exposure level. The analytical techniques that will be applied are the neutron activation joined to related non nuclear analytical techniques, such as atomic absorption.

2. INTRODUCTION

The industrial processes introduce the contamination risks to the workers all the time. The easiest ones to be identified are those that kill or mutilate. Other processes take time to produce the sinister effects, because of that the contamination is difficult to be identified.

There are around 15000 chemical and physical toxic agents commonly used in industries but there are only some legal rules of exposition to 500 of them. Thus the effects throughout the years and the biggest part of these effects hasn't been demonstrated. It is important to say that every day, with more modern processes, new chemical agents appear enlarging the list of pollutants. The effects of these pollutants are unknown.

In Brazil the statistical surveys about professional diseases refer to the accidents and damages and not to the occupational diseases developed through long exposures to unhealthy conditions of work, with physical risk and toxic chemical substances. The many cases of occupational diseases that are computed are those that were reached in extremely dangerous conditions or damages. The workplace exposures are computed when the acquisition of disease is obvious or probable, that is, dangerous diseases easily identified. But the great part of workers is exposed to low levels that can be lethal in a long period of time, because these expositions may cause chronic infirmities. Most of the times the outset of the diseases is not noticed and the appearing of a pulmonary cancer or heart diseases is attributed to non-occupational causes by the industry, by the medical group. Then these diseases are not computed.

Among the toxic substances, the metals are detached because many of them are already present on the work environment and may cause since allergies until cancer and many dangerous intoxications. The Law nº 24 (29th December, 1994) from the Secretaria de Segurança e Saúde no Trabalho (Security and Health at Work Secretary) approved the NR-7 Program of Medical Control of Occupational Health, in what the Maximum Biological Levels Allowed and the Values of Normality References are previewed. Concerning metal and toxic inorganics only the arsenic, chromium, cadmium, lead and mercury values are previewed. Manganese, for instance, that is not mentioned, presents a biological half-life of 37 days, being the bones and the brain the slowest places of removing. One of the consequences of its accumulation in the body is the muscular hypertonie of the face and of inferior limbs. Other metals are not mentioned either.

Biological monitors of exposure assess the health risk through the evaluation of the level of incorporation or exposure. The biological materials more frequently used for the monitoring of metals are blood, urine, hair, nails, expired air, faeces, milk, and others.

This Project will be developed at CDTN (Centro de Desenvolvimento da Tecnologia Nuclear) and partners: FUNED (Fundação Ezequiel Dias), CST/SMSa (Secretaria Municipal de Saúde de Belo Horizonte) and FUNDACENTRO/BH.

In CDTN a broad spectrum of nuclear and non-nuclear technical activities were conducted, related to the fields of ore prospecting, petrography, mineral processing, chemical processes, uranium enrichment, material testing, fuel element development, waste management, fuel reprocessing, reactor physics, accident analysis, reactor commissioning, thermal-hydraulic testing, electric-mechanical systems design, environmental engineering, radiation protection, licensing, irradiation, radioisotope application, chemical analysis, mechanical systems construction, electronics, instrumentation development, nuclear measurements, computing, data processing, documentation and education.

The facilities occupy around 25,000 square meters located on a tract nearly 200,000 square meters, where about 400 employees are presently at work. As far main irradiating apparatus are concerned the facility a 7×10^3 MBq irradiator of ^{60}Co , a natural uranium metal fuelled light water moderated sub-critical assembly and the TRIGA MARK I reactor. There is a strong and mutually profitable co-operation with national and foreign nuclear centers, universities, institutions, associations and industries. Through the years CDTN has been determining chemical elements in many different matrixes including air filters and biological materials through the technique of neutron activation (NAA) (parametric analyses k_0 - standard method and non-parametrical) involving or not chemical and/or radiochemical separations using the rotary specimen rack of the TRIGA MARK I IPR R1. Analytical techniques such as atomic absorption (AA), visible ultraviolet (UV-VIS), gas chromatography (GC), x-ray (XR), HPLC and others, constitute an available instrumental group monitored by an expert staff.

The Fundação Ezequiel Dias/FUNED (Ezequiel Dias Foundation) is a public state organization involving several institutes. In the Octavio Magalhães Institute there is the Divisão de Bromatologia e Toxicologia (Division of Toxicology) responsible for the food and the biological materials analysis.

The Coordenação de Saúde do Trabalhador/CST/SMSa (Worker Health's Co-ordination) is an sector in Secretaria Municipal de Saúde de Belo Horizonte (Municipal Health Secretary). It's responsible for planning and co-ordination of the worker's health policies in the city of Belo Horizonte. This sector works with social assistance (the workers who have occupational diseases are cared by a team including physicians, social assistants, nurses, physiotherapists, and receive complete treatment) and workplace's surveillance, which means the investigation of the workplace's hazard and the implementation of control measures.

The FUNDACENTRO/BH is linked to Administração Pública Federal-Ministério do Trabalho (Federal Administration-Work's Ministry). The main tasks of this department are to develop researches and to give instructions in the work scope and the relations with health and security.

This Project is inserted in the work/studies developed by CDTN, FUNED, CST/SMSa and FUNDACENTRO/BH. It has been developing some studies about the monitoring of working places and occupational diseases, such as the evaluation of risky factors associated to the exposures to lead in battery reformer places by CDTN, FUNED, CST/SMSa and FUNDACENTRO/BH, having other partner, the Secretaria Municipal de Saúde de Contagem (Municipal Health Secretary of Contagem).

On the other hand, the CDTN, among its objectives, has been giving priority to the projects about the environment and health:

- "Study of the sorption of caesium in the soil" (funded by Conselho Nacional de Pesquisa/CNPQ - National Research Council),
- "Physical and mathematical modelling of contaminant transport in aquifers" (funded by IAEA),
- "Study of contamination by mercury in manual gold mines in Minas Gerais: its impact on health and on environment" (partnership: CDTN, Fundação Estadual do Meio-Ambiente/FEAM - Environmental Foundation of State of Minas Gerais, Fundação Nacional de Saúde/FNS - Health National Foundation),
- "Study of parameters related to the quality of the water consumed by the population of 56 cities of the State of Minas Gerais - Brazil" (was presented to IAEA in 1993; partnership: CDTN, Fundação Estadual do Meio-Ambiente/FEAM - Environmental Foundation of State of Minas Gerais, Fundação Nacional de Saúde/FNS - Health National Foundation),
- "Mercury in manual gold mines" (partnership: CDTN - FEAM - Secretaria Estadual de Saúde/SES - Health Secretary of State of Minas Gerais).

Relating environmental analysis, CDTN has been managing and executing Environmental Monitoring Programs involving mining, industries and nuclear facilities. The Institute has around of 4500 dosimeters films users per month in 270 institutions (hospitals, industries, research institutes), distributed all over the Country.

3. OBJECTIVE

The overall objective of this Project is to make a survey of the exposures to metals related to occupational diseases in galvanizing industry using as bioindicators, hair, nails, blood, urine, and individual air filters. These matrixes will indicate the incorporation of metals and the exposure level. Besides arsenic, chromium, cadmium, lead and mercury, also zinc, aluminium, tin, nickel, copper, cobalt, manganese and vanadium will be determined if present in the samples.

This Project will be the first evaluation of metals in occupational environment in the State of Minas Gerais, determining the elements in bioindicators and personal filters using nuclear and related analytical techniques.

4. STUDY AREA

Belo Horizonte, the capital of the State of Minas Gerais and its neighbourhood are the second industrial center of Brazil, concentrating many industries in several areas: metallurgy of iron, textile, automotive, refractory-materials, ink, food, mining, ceramics and cement plant. Considering the hazards involving chemical elements, metals predominate the health's problems in worker of different

plants. But there are no registers about the level of metal concentration in the environmental air in industry, nor even of the level of workers' contamination.

Besides those works there are around 30 galvanization industries from those called home industries to modern ones in Belo Horizonte. Many of them are in the commercial center of the city and this kind of industry is responsible for the majority of metal contamination occurrences.

Galvanizing industry is an electroplating process where the process of depositing a coating having a desirable form is by means of electrolysis. Its purpose is generally to alter the characteristics of a surface so as to provide improved appearance, ability to withstand corrosive agents, resistance to abrasion, or other desired properties or a combination of them although occasionally it is used simply to alter dimensions.

Electrolysis is carried out in a bath which may consist of fused salts or solutions of various kinds; in commercial practice it is almost invariably a water solution.

In general the steps in galvanization are: polishing using abrasives, washing with acids and sodium hydroxide and electrodeposition involving deposits of aluminium, cadmium, chromium, cobalt, copper, gold, indium, iron, lead, nickel, platinum, silver, tin and zinc.

Because of the variety of metals used in galvanizing process the four institutions, CDTN, FUNED, CST/SMSa and FUNDACENTRO/BH, as partners, will examine which metals are more critical in terms of exposure.

5. EXECUTION

The sampling of the workers' biomaterials will be carry out by the institutions. The control group, formed by people that aren't exposed to the same environmental that the workers, will be selected and the institutions will collect the samples.

The analysis of the reference materials and the bioindicators and personal air filters samples from the workers and the control group will be performed by CDTN and FUNED. The techniques that will be used are NAA, XR, that will be executed by CDTN and other techniques such as AA, HPLC, UV-VIS, GC that will be executed joined with CDTN and FUNED whenever necessary.

The results will be evaluated by CDTN, FUNED, CST/SMSa and FUNDACENTRO/BH considering the physicochemical properties of metals, ventilation parameters and permissible levels in biological media, biological limit values or biological versus exposures values. Under medical point of view solutions will be suggested.

6. PRELIMINARY RESULTS

Some preliminary results are in TABLE I and II. The samples are hair and nails from the 9 workers of a small industry in the center of Belo Horizonte: 3 officers, 2 bath operator, 1 metal piece washer and 3 polishers.

The hair and nails samples were irradiated without washing for 5 min to detect the short life nuclides. It was applied the neutron activation, k_0 parametric neutron activation analysis method. The objective of analysing without washing was to verify the level of exposition. Quality control was done using replicates of samples and the certificate reference material Human Hair (GBW 09101), from Shanghai Institute of Nuclear Research Academia Sinica.

In TABLE I are the concentrations determined in the hair samples and in TABLE II are the concentrations found in the nails. The results are in function of the occupation of the worker. It wasn't possible, during the sampling, to collect hair and nails from everybody because of several problems: one was bald, the other one had cut the nails the day before, and so on. It's possible to observe that the concentrations determined in workers samples are higher than in reference material.

TABLE I – CONCENTRATIONS OF ELEMENTS IN HAIR (H)
($\mu\text{g g}^{-1}$)

	Al	Cl	Cu	I	Mn	Na	Ti	V
Officer 1	485 $\pm$ 27	1157 $\pm$ 150	68 $\pm$ 33	5 $\pm$ 2	9 $\pm$ 4	758 $\pm$ 106	*	*
Zn bath operator	644 $\pm$ 45	1786 $\pm$ 387	116 $\pm$ 35	*	*	562 $\pm$ 122	*	*
Cr, Cu and Ni bath operator	134 $\pm$ 12	942 $\pm$ 87	82 $\pm$ 22	*	5 $\pm$ 3	880 $\pm$ 67	*	*
Piece washer	450 $\pm$ 20	728 $\pm$ 90	140 $\pm$ 23	*	6 $\pm$ 3	478 $\pm$ 58	*	*
Polisher 1	3417 $\pm$ 67	1930 $\pm$ 200	400 $\pm$ 60	*	22 $\pm$ 6	625 $\pm$ 100	84 $\pm$ 40	2.1 $\pm$ 0.8
Polisher 3	538 $\pm$ 28	307 $\pm$ 80	132 $\pm$ 30	*	12 $\pm$ 3	610 $\pm$ 78	*	*
HH (experimental)	14 $\pm$ 7	157 $\pm$ 50	19 $\pm$ 18	*	4 $\pm$ 2	269 $\pm$ 48	*	*
HH (certificated)	13.3 $\pm$ 2.3	152**	23 $\pm$ 1.4	0.875**	2.94 $\pm$.20	266 $\pm$ 12	-	0.069**

*not detected

** information values

TABLE II – CONCENTRATIONS OF ELEMENTS IN NAILS (N)
($\mu\text{g g}^{-1}$)

	Al	Cl	Cu	I	Mn	Na	Ti	V
Zn bath operator	776 $\pm$ 100	457 $\pm$ 290	188 $\pm$ 96	*	*	1146 $\pm$ 258	*	*
Cr, Cu and Ni bath operator	1540 $\pm$ 200	3420 $\pm$ 450	1210 $\pm$ 135	17 $\pm$ 8	14 $\pm$ 1	1390 $\pm$ 340	*	*
Polisher 1	16500 $\pm$ 200	8770 $\pm$ 880	990 $\pm$ 200	*	99 $\pm$ 20	2100 $\pm$ 500	210 $\pm$ 170	10 $\pm$ 4
Polisher 2	660 $\pm$ 190	9130 $\pm$ 700	1040 $\pm$ 180	*	*	1830 $\pm$ 380	*	2 $\pm$ 3
Officer 2	275 $\pm$ 100	2215 $\pm$ 650	*	*	*	610 $\pm$ 380	*	*

*not detected

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**A STUDY ON ENVIRONMENTAL POLLUTION
MONITORING AND OCCUPATIONAL
HEALTH IN THE CAPITAL IRON AND STEEL
COMPANY, BEIJING, CHINA, USING
NUCLEAR AND RELATED ANALYTICAL
TECHNIQUES**

Research Institute:

Institute of High Energy Physics and Laboratory of Nuclear
Analysis Techniques, Academia Sinica, Beijing 100080, China

Chief Scientific investigator:

Chifang Chai

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A STUDY ON ENVIRONMENTAL POLLUTION MONITORING AND OCCUPATIONAL HEALTH IN THE CAPITAL IRON AND STEEL COMPANY, BEIJING, CHINA, USING NUCLEAR AND RELATED ANALYTICAL TECHNIQUES

**Chifang Chai ^{1)*} Xiaolin Hou¹⁾ Qinfang Qian¹⁾, Wenjun Ding¹⁾
Xiangqian Feng¹⁾ Minxu Kuang²⁾ Hongyu Wang²⁾ Yongchen Zhang²⁾**

**1) Institute of High Energy Physics and Laboratory of Nuclear Analysis
Techniques, Academia Sinica, Beijing 100080, P.R. China**

2) General Hospital of the Capital Iron and Steel Company, Beijing, P.R. China

* Chief Scientific investigator

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ABSTRACT

The atmosphere pollution in some Chinese cities is becoming more and more serious with the industrial development in the past decades. The airborne particulate concentration in Beijing, the Capital of China, far exceeds the allowable level set by the Chinese government and by the related international organizations. The main contribution source for the Beijing atmospheric particulate is the Capital Iron and Steel Company, which constitutes 55% of total air-borne particulate in Beijing. In the framework of this CRP organized by IAEA, we select this company as a target workplace. The INAA (instrumental neutron activation analysis), PIXE (proton induced X-ray emission analysis), SRXRF (synchronous radiation X-ray fluorescence spectrometry) and other related techniques will be applied to determine the concentrations of some target elements, e.g. heavy metal and toxic elements, in

environmental samples (including airborne particulate, soil and plants) and human samples (including head hair, urine and blood) collected from this company, its surrounding region and a non-polluted region as a control. The activity completed at the first year and the working plan for next year is outlined in this report. Other related information will be dealt with as well.

1. INTRODUCTION

The Capital Iron and Steel Company is one of the biggest industrial companies in Beijing, China. The environmental pollution (especially heavy metal and toxic element pollutants) is very serious in workplace and surrounding regions[1,2]. More than 55% atmospheric particles in the Beijing city come from this company. There are more than 100,000 people working in this company and over 500,000 people living in its surrounding region. Thus, the investigation of trace element level, especially of heavy metal and toxic element level, in the environmental materials in the workplace, surrounding region and human tissues of workers and local residents is highly needed for the evaluation of environmental pollution level in workplace and surrounding regions and its impact on occupational health status.

The concentration of airborne particulate matter in atmosphere and the contents of heavy metal and toxic elements in it can directly reflect the environmental pollution level. In addition, some plants can also be used as bioindicator to monitor environmental pollution level[3]. The contents of pollutants in hair, nail, urine and blood can indicate the level and absorption status of pollutants in human body. Due to its simplicity of sampling, preparation and analysis, human hair is usually used for monitoring long-term environmental exposure to pollutant as well as for evaluating poisoning caused by heavy metals[4], because elements are absorbed by hair and retained over a period of time they remain in the head, while blood and urine for transient environmental exposure to pollutant. In this work, airborne particulate matter, plants, soil, human hair, blood and urine are selected to study the environmental pollution level and occupational health in the Capital Iron and Steel Company, Beijing, China.

2. RESEARCH PROJECT

The intended project bears on the environmental pollutant monitoring in the Capital Iron and Steel Company, Beijing, and its effects to occupational health of the workers exposed to the workplace. The following research contents will be included:

2.1 Sampling

Environmental samples: airborne particulate matter, plants and soil

Human tissues: hair, urine, blood and organ tissues (if possible)

2.2 Analysis

Analytical methods:

The nuclear analytical techniques, such as neutron activation analysis(NAA), proton induced X-ray emission (PIXE), synchronous radiation X-ray fluorescence(SRXRF), scan proton microprobe(SPM) and related techniques are available for the determination of elements.

Target elements:

Au, As, Br, Cd, Cu, Co, Cr, Fe, Hg, I, In, Mn, Ni, Pb, S, Sb, Sc, Se, V and Zn

2.3 The investigation of effect of environmental pollution of workplace on occupational health of workers and local human health

Comparing the environmental pollution status with the level of toxic and excessive essential elements in human tissues in workplace and surrounding region, the effect of environmental pollutants in workplace to occupational health of workers can be studied.

2.4 Study on the transfer model of toxic elements in environment

Emphasize will be put on the transfer of the volatile and mobile elements from environment into human body.

3. WORK DONE AND BEING DONE AT THE FIRST YEAR

3.1 Selection of appropriate sampling locations for collecting human tissue samples

The Capital Iron and Steel Company is located in the west of Beijing city (Fig. 1), more than 100,000 people work there, with over 500,000 people living in its surrounding region with 5 km radius. The company consists of an ironworks, 3 steelworks and other auxiliary works, in which the ironworks include 4 iron-smelting furnaces. The environmental pollution in ironworks is the most serious in all works of

the company. More than 3000 people work in the ironworks, and more than 500 work in each of iron-smelting furnaces.

In this work, two of 4 iron-smelting furnaces are selected to investigate the environmental pollution, and 25 workers, all furnacemen, are selected from each iron-smelting to collect human tissue samples and to investigate their occupational health status. As a comparison, the same human tissue samples are collected from 50 rear-service or administrative staffs working in the same works.

As the surrounding region, Institute of High Energy Physics, located no 5 km east of the company, is selected for collecting air particulate matter, plants and soil samples. Human tissue samples are also collected from the people working in this institute, who are scientific researcher or administrative staffs without any direct contact of pollutants.

As the non-polluted region, Xinzhen, located on more than 20 km southeast of the company is selected. The local residents are selected to collect human tissue samples.

3.2 Collection and preparation of environmental and human tissue samples

The airborne particles are collected at selected sites in Beijing area by using high-volume air sampler in different seasons. Millipore filter is used to collect airborne particles, in which the contents of impurity elements are very low. Some plants samples, such as tree leaves and grass, are collected as biomonitor samples to investigate the level of environmental pollutants.

According to the recommendation of IAEA for sample collection, about 3 grams of human hair are collected from the occipital part to enable several analysis. Precleaned stainless steel scissors and trimmers are used for collection of specimens, and clean paper bags are used for sample storage. The head hair samples are washed with acetone and deionized water and air-dried according to the procedure recommended by IAEA for human hair[5]. Before cleaning, hair is cut into about 3 mm long pieces.

When the human hair samples are collected, 5 ml of blood and 30 ml of urine samples are collected simultaneously into a clean polyethylene vial (acid-washed and cleaned with high purity water). The serum is separated from blood in 5 hours after collection of samples, and stored in -20. The urine is freeze-dried and stored in refrigerator.

The collection of all human tissue samples has been finished.

3.3 Validation of analytical methods

Neutron activation analysis (NAA) is a sensitive method for the determination of many elements. In Beijing, there are 3 reactors available: a heavy-water reactor (HWR) with the maximum neutron flux of $810^{13} \text{ n cm}^{-2} \text{ s}^{-1}$, a swimming pool reactor (SPR) with $210^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ and a Miniature Neutron Source Reactor (MNSR) with $110^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. In MNSR, a pneumatic transfer system can be conveniently applied to determine the elements with short-lived nuclides, such as V, Ti, In, Mn, Se, Br and I[6]. For other elements, such as Hg, As, Cr, Zn, Co, Se, Fe, Sb, Sc, Ni, Cd and Au, HWR is more suitable.

The radiation detection system consists of 5 HpGe detectors with energy resolution of 1.8 to 2.0 keV at ^{60}Co 1332.5 keV and one planar HpGe detector with good energy resolution for lower energy gamma ray. The PC-based multichannel analyzer and automatic sample changer are well equipped.

A two-dimensional scanning unit with size-adjustable slit from 5050 μm to 11 mm in the Beijing Electron-Positron Collider (BEPC) at IHEP with 2.2-2.8 GeV energy and 150 mA maximum current intensity is used to study the distribution patterns of trace elements in two-dimensional space. In addition, the contents of Pb and S can also be determined using this method, which can not be determined by NAA in low content samples.

For Pb, S and Ni, proton induced X-ray emission (PIXE) can be applied in a Van de Graaff accelerator at IHEP[7]. In addition, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, As, Se and Br are also determined with PIXE, and the analytical results will be compared with those of NAA.

The validation of NAA has been carried out by analysis of three standard reference materials, such as NIST-1633a (coal fly ash), GBW-07601 (human hair) and GBW-09101 (human hair). The analytical results are listed in Table 1 with the certified values.

Table 1 Analytical results of 2 standard reference materials by INAA

Element	GBW-07601 $\mu\text{g/g}$		GBW-09101 $\mu\text{g/g}$		NIST-1633a $\mu\text{g/g}$	
	this work*	certified values	this work*	certified values	this work *	certified values
As	0.23 $\pm$ 0.07	0.28 $\pm$ 0.05	0.56 $\pm$ 0.09	0.59 $\pm$ 0.07	147 $\pm$ 6	145 $\pm$ 15
Br	0.35 $\pm$ 0.08	0.36	0.58 $\pm$ 0.05	0.602	2.2 $\pm$ 0.3	
Cd		0.11 $\pm$ 0.03		0.095 $\pm$ 0.012	1.12 $\pm$ 0.20	1.0 $\pm$ 0.15
Co	0.069 $\pm$ 0.008	0.071 $\pm$ 0.012	0.131 $\pm$ 0.010	0.135 $\pm$ 0.008	44 $\pm$ 3	46
Cr	0.38 $\pm$ 0.06	0.37 $\pm$ 0.06	4.78 $\pm$ 0.33	4.77 $\pm$ 0.48	203 $\pm$ 7	196 $\pm$ 6
Cu	11.3 $\pm$ 1.4	10.6 $\pm$ 1.2	23.4 $\pm$ 2.5	23.0 $\pm$ 1.4	120 $\pm$ 6	118 $\pm$ 3
Fe	49 $\pm$ 7	54 $\pm$ 10	73.8 $\pm$ 4.8	72.2 $\pm$ 6.6	9370 $\pm$ 120	9450 $\pm$ 100
Hg	0.39 $\pm$ 0.09	0.36 $\pm$ 0.08	2.08 $\pm$ 0.18	2.16 $\pm$ 0.21		0.16 $\pm$ 0.01
I			0.874 $\pm$ 0.017	0.875	3.50 $\pm$ 0.36	
In					157 $\pm$ 11	
Mn	6.8 $\pm$ 0.6	6.3 $\pm$ 0.8	2.98 $\pm$ 0.12	2.94 $\pm$ 0.20	204 $\pm$ 20	190
Ni		0.83 $\pm$ 0.19		3.17	123 $\pm$ 12	127 $\pm$ 4
Sb	0.093 $\pm$ 0.009	0.095 $\pm$ 0.016	0.24 $\pm$ 0.02	0.21	6.8 $\pm$ 0.4	7
Sc	0.010 $\pm$ 0.002	0.008 $\pm$ 0.001	2.80 $\pm$ 0.22	2.87	39 $\pm$ 4	40
Se	0.57 $\pm$ 0.05	0.60 $\pm$ 0.04	0.59 $\pm$ 0.06	0.58 $\pm$ 0.05	9.7 $\pm$ 0.9	10.3 $\pm$ 0.6
V			0.065 $\pm$ 0.006	0.069	298 $\pm$ 8	300
Zn	203 $\pm$ 12	190 $\pm$ 9	186 $\pm$ 7	189 $\pm$ 8	237 $\pm$ 17	220 $\pm$ 10

* Average value and standard deviation of 3 determinations

4. PLAN FOR FUTURE WORK

4.1 Collection and preparation of all environmental and human tissue samples

4.2 Analytical quality assurance

Three methods to guarantee the analytical quality will be used. (1) In-house working materials; (2) Standard or certified reference materials. Various environmental and biological reference materials made in USA, IAEA and China are available, e.g. human hair, blood, serum, freeze-dried urine, soil, air particulate, plants etc. (3) External intercomparison.

4.3 Optimization of nuclear analysis techniques

The optimal parameters for INAA, PIXE and SRXRF will be selected via a series of preliminary experiments.

4.4 Analysis and data evaluation

Next year, we will analyze part of the environmental and human samples collected from the target area by INAA and PIXE.

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**CO-ORDINATED RESEARCH PROGRAMME
ASSESSMENT OF LEVELS AND HEALTH-EFFECTS OF AIRBORNE PARTICULATE
MATTER IN MINING, METAL REFINING AND METAL WORKING INDUSTRIES USING
NUCLEAR AND RELATED
ANALYTICAL TECHNIQUES**



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NUCLEAR PHYSICS INSTITUTE
CZ-250 68 REZ NEAR PRAGUE
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MONITORING OF EXPOSURE TO SELECTED METALS IN WORKERS OF A FERROALLOY PRODUCTION PLANT USING NAA AND PIXE

J. KUCERA¹, V. BENCKO², E. FABIÁNOVÁ³, J. SYSALOVÁ⁴, V. HAVRÁNEK¹,
V. HNATOWICZ¹

¹Nuclear Physics Institute, CZ-250 68 Rez near Prague, Czech Republic

²Institute of Hygiene and Epidemiology, 1st Medical Faculty, Charles University, Studnickova 7, CZ-128 00 Prague 2, Czech Republic

³Special State Health Institute, K nemocnici 1, SK-975 56 Banská Bystrica, Slovakia

⁴Institute of Analytical Chemistry, Trace Element Laboratory, Geologická 6, CZ-152 00 Prague 5, Czech Republic

ABSTRACT

Advantages and pitfalls of direct and biological monitoring of occupational exposure are briefly mentioned and a project aimed at evaluating exposure to chromium (and possibly manganese) in workers of a ferro-alloy production plant using both the above approaches is outlined. Facilities for NAA and PIXE at the Nuclear Physics Institute at Rez to be used in the project are described. Results of quality assurance of INAA method for analysis of workplace air born particulate matter and blood sampling are presented. Results from previous work relating to this Co-ordinated Research Programme - studying exposure of workers of a vanadium pentoxide production plant are also briefly reviewed.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

In connection with the prevention of the adverse health effects of harmful substances in occupational and environmental settings, there is a growing need to harmonize activities in the field of toxicological methodology and approaches to risk assessment [1]. The results of direct monitoring, i.e. the assessment of exposure from a concentration in air, water, food, workplace, etc., may be misleading, if various mechanisms of intake and/or absorption lead to a different burden of the organism, if multiple mechanisms of intake are to be considered, and especially if short- and long-term effects are to be distinguished [2]. Therefore, in the assessment of health risk arising from environmental, occupational and accidental exposure to toxic metals and other substances, the use of biological monitoring is steadily increasing [3-5]. This approach is facilitated if reliable biological indicators of exposure, such as changes of a concentration of the substance of interest, its metabolites, and other specific species in indicator or target tissues, are well established.

Both approaches will be used to study exposure in workers of a ferro-alloy production plant in Slovakia (at Istebné, the Orava region) where alloying compounds for the steel industry, such as ferrochromium, ferromanganese, ferrosilicon, etc. are produced. Exposure to chromium will be of the main concern owing to allergic and carcinogenic effects of the element in the Cr^{VI} form. Toxicity of chromium is mainly due to Cr^{VI} that can be absorbed mainly by the respiratory tract. Chromium compounds are also easily absorbed through the skin. Besides direct monitoring of exposure by determining a chromium concentration in the workplace air, the element concentration in serum, erythrocytes, urine, hair and nails will be studied in exposed and control persons. In serum chromium occurs as Cr^{III} and is bound to serum proteins, especially transferrin and albumin. The hexavalent chromium absorbed during inhalation rapidly penetrates the erythrocyte membrane, is then reduced to Cr^{III} and binds predominantly to haemoglobin [6]. Thus, a ratio of chromium concentrations in serum and erythrocytes in exposed persons may provide useful information about dynamic changes of the element concentrations during exposure. Chromium in urine measurements appear the most suitable indicator for biological monitoring [6], while the element content in hair and nails may provide additional information about the chromium exposure.

Exposure to manganese, which has adverse effects on the central nervous systems and the lungs, may be studied in a similar manner as well. This will depend on availability of a facility for short-time irradiation for NAA which is presently being reconstructed.

2. METHODS

2.1 Sampling and sample handling

A respirable portion of air particulate matter (APM) in the workplace air will be collected in two size fractions with the aid of personal samplers (SKC, USA) with PM10 and PM2.5 inlets.

Analytical requirements for measurement of both elements in blood and urine are very stringent, because there is a high risk of contamination on sampling and sample handling. A stainless steel needle cannot be used for blood collection. Therefore, needles siliconized on the inside from two producers (SARSTEDT, BECTON DICKINSON) that are recommended for trace element analysis were tested, as well as collection vials from both producers, i.e. plastic S-Monovette® vials and siliconized glass Vacutainer® vials, respectively. The test were performed by simulating blood collection from acid-washed polyethylene (PE) vials which contained serum obtained by reconstitution of Versieck's 2nd Generation Biological Reference Material (uncontaminated freeze-dried human serum) [7] with certified concentrations of chromium and manganese. The serum was reconstituted with demineralized water in an acid-cleaned polyethylene (PE) vial and warmed up to 37°C. Then, blood sampling was simulated by puncturing the PE vial with the needle and by collecting 5 mL of the reconstituted serum which was subsequently left in the collection vial for 1 hour. Chromium and manganese contents in the serum were determined by ET-AAS at the Institute of Analytical Chemistry, Trace Element Laboratory, Prague, in Class 100 environment, because the Rez nuclear reactor was out of operation for a considerable part of 1997.

Real sampling and sample handling prior to analysis will be performed in class 10 environment provided by prefilters and ULPA filters contained in a transportable module for air filtration (Holten, Denmark). Prior to collection of venous blood, cleaning of the skin will be performed with deionized water and ethylalcohol, because both chromium and manganese are excreted by sweat in concentrations that exceed those found in serum of normal persons several times [6]. After separation of serum and erythrocytes, both blood components will be freeze-dried prior to analysis.

Spot samples of urine will be collected in acid-washed PE vials and freeze-dried as well.

Hair and nail samples will be cut with scissors and/or a clipper and external contamination will be removed by the IAEA standardized procedure [20] and by an adapted IAEA procedure, respectively, which has been described elsewhere [2].

2.2. Analytical methods

2.2.1. Neutron activation analysis

Instrumental neutron activation analysis (INAA) and proton induced X-ray emission (PIXE) will be used for analysis of APM samples, while radiochemical neutron activation analysis (RNAA) will be employed for low level determination of Cr (and possibly Mn) in biological samples.

For INAA and RNAA, facilities for both short- and long-time irradiations are available at the LWR-15 nuclear research reactor of the Nuclear Research Institute Rez, plc. in which a thermal neutron fluence rate of $8 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ is available. Gamma-ray spectrometric measurements are performed using several HPGe detectors with relative efficiency ranging from 11 to 52% and a FWHM resolution of 1.75 to 1.85 keV (both for the 1332.4 keV photons of ^{60}Co) and a well-type HPGe detector with an active volume of 125 cm³ and the FWHM resolution of 1.95 keV. Several software packages for gamma-ray spectra evaluation (NUCLEAR DATA software, DEIMOS [8], HYPERMET for PC [9]) and calculation of the final results (ND software, KAYZERO/SOLCOI [10]). INAA procedures will be used similar to those validated for analysis of APM samples in ambient air that have already been described earlier [11]. For low level determination of chromium, a

RNAA procedure developed by Greenberg and Zeisler [12] is presently being adapted, while another RNAA procedure for low level determination of manganese in biological samples has been developed in our laboratory earlier [13].

2.2.2. PIXE

The following PIXE experimental set-up is available at the NPI. A beam of protons with the energy of 1.31 MeV and 2.35 MeV is obtained from a Van de Graaff accelerator. The lower energy is more suitable for the excitation of elements with lower atomic numbers (up to Mn), whereas the higher energy is favourable for determination of elements with higher atomic numbers. The beam collimated to a diameter of 5 mm enters a vacuum target chamber after passing through a thin Al diffusion foil which is used as part of a monitoring system and simultaneously, to improve the homogeneity of the beam. In this arrangement, a relatively high irradiation current can be used and the influence of the possible sample micro-homogeneity is reduced. The bombardment is performed to achieve a collected charge of 10 μC and 50 μC for the lower and higher energy of protons, respectively. The chamber is equipped with a sample changer for 7 samples fixed in standard polyframes. Characteristic X-rays induced by protons are allowed to leave the chamber through a thin exit window formed by a 10 μm mylar foil and are measured employing a Si(Li) detector (active area 80 mm^2) with a Be window coupled to a Canberra ACCUSPEC PC-based analyser through the standard associated electronics. A sample-to-detector distance is 30 mm, the FWHM energy resolution of the system amounts to 180-190 eV for the 5.9 keV X-rays of Fe. Outside the chamber, between the exit window and the detector, a suitable X-ray attenuation filter can be inserted. Determination of a proton dose is carried out by measuring a number of protons scattered from the Al foil using a surface barrier Si(Au) detector connected to a separate counter. For the X-ray spectra evaluation, a programme package PIXE-NPI developed at the NPI is available.

3. RESULTS

3.1. Quality assurance of the present study

Great care is devoted to quality assurance of both sampling and analytical stages of the project to be able to arrive at valid results. Quality assurance of air pollution studies is hampered by lack of suitable certified reference materials, i.e. air particulate matter (APM) on a filter. In our previous INAA studies we have been using small 0.5 mg to 15 mg aliquots of NIST SRM 1648 Urban Particulate matter. Our results for chromium and many other elements agreed well with the NIST certified or information values [14]. This demonstrates excellent homogeneity of NIST SRM 1648 for much smaller masses than 100 mg which is a minimum given in the certificate and also very good stability of our analytical system. However, for manganese (and vanadium) our values have been by about 10% lower compared to the NIST information (certified) values, but in agreement with those compiled from the literature by Gladney et al. [15]. Therefore, we decided to elucidate these discrepancies in detail by optimizing the irradiation and counting conditions for determining these two elements and to perform simultaneous analysis of other NIST SRMs and BCR CRMs of environmental and biological origin with contents of the investigated elements of the same order of magnitude as in NIST SRM-1648. Experimental details have already been given elsewhere [14]. Results of Mn determination in the samples investigated are summarized in Table 1 where the mean values and their combined uncertainties are given.

Table 1. Manganese contents in biological and environmental reference materials

Reference material	Mn content, mg kg ⁻¹ (dry weight)			
	This work Mean ± unc. ^a (N)	Previous NPI results Mean ± SD (N)	Certified or information value ^b	Literature value [15]
NIST SRM-1648 ^c	768 ± 18 (4)	770 ± 46 (27)	860	822 ± 45 (19)
NIST SRM-1648 ^d	768 ± 23 (4)			
NIST SRM-1648 ^e	795, 791 (2)			
NIST SRM-1633a	185 ± 17 (4)	-	179 ± 8	188 ± 20 (43)
NIST SRM-2704	570 ± 17 (4)	566 ± 46 (6)	555 ± 17	550 ± 50 (9)
BCR CRM 038	479 ± 7 (4)	-	479 ± 16	-
BCR CRM 101	908 ± 20	-	915 ± 11	-
BCR CRM 143	930 ± 27	-	904 ± 13	-

^a - combined uncertainty

^b - certified values are those associated with uncertainties

^c - about 5 mg aliquots from bottle A

^d - about 5 mg aliquots from bottle B

^e - two aliquots of about 100 mg from bottles A and B

Obviously, excellent agreement was obtained between our previous results in small aliquots of NIST SRM-1648 and values obtained in this study, including the results for about 100 mg-aliquots of this material. The precision of Mn determination was significantly improved. Excellent homogeneity of this material for sample masses of about 5 mg was again confirmed. Our results also compared well within the uncertainty margins with certified and/or information values for other NIST SRMs and BCR CRMs studied. Therefore, two conclusions can be derived from results of this study. First, agreement of our results with certified and/or information values in the NIST SRMs and BCR CRMs analyzed, except for NIST SRM-1648, suggests that these values are mutually traceable, because INAA is known as an analytical technique without the measurable matrix dependence for many matrices. On the other hand, the previously found discrepancies between our results and the NIST values for manganese and vanadium in SRM-1648 were confirmed for both 5 mg and 100 mg sample masses which suggests that the NIST values are positively biased by about 10% and a similar bias has also been found for vanadium [14]. The same conclusion can also be derived from a comparison of the NIST values with those compiled from the literature by Gladney et al. [15] and with those determined by INAA by Greenberg [16]. Finally, it can be mentioned that besides very well known advantages of neutron activation analysis for certification of element contents in reference materials, a special capability of INAA for establishing the mutual traceability of certified element values in reference materials with different matrices has been demonstrated.

In case of chromium and manganese determination in human blood and urine, it is not only a problem of quality assurance of analysis, but also quality assurance of sampling and sample handling, i.e. preventing contamination, which makes the accurate determination of very low levels of the elements a challenging analytical task. Therefore, the blood sampling devices produced by SARDSTET and BECTON DICKINSON companies, i.e. disposable steel needles siliconized on the inside surface and collection vials designated for "trace metal analysis", were tested for extraneous additions of both elements. It has been obvious from the producer data that the possible maximum amounts of elements that are guaranteed by both producers would prevent determination of normal levels of both chromium and manganese in blood and its derivatives. This is demonstrated in Table 2 where the maximum amounts of elements possibly released from the collection devices are given and compared with those in serum of occupationally unexposed persons provided that 5 mL of blood are

collected. Moreover, the maximum extraneous additions for the Vacutainer® tubes and needles may be underestimated, because a higher contamination is to be expected on blood sampling than this caused by “water extractable” concentrations, due to complexing properties of blood aminoacides and peptides.

Table 2. Comparison of the possible extraneous element additions on blood sampling using S-Monovette® for metal analysis, SARSTEDT, and Vacutainer® for trace element analysis, BECTON DICKINSON, with the normal levels in serum

Element	Max. extraneous addition according to the producers leaflets (µg/L)		Resulting value in serum ^b (µg/L)		Normal serum value (µg/L) [6, 17]
	Monovette® ^a	Vacutainer® ^b	Monovette® ^c	Vacutainer®	
Al	40	-	8.0	-	1.3 - 1.6
Cd	1.5	0.6	0.3	0.6	0.1 - 0.2 ^d
Cr	5.0	0.9	1.0	0.9	0.1 - 0.2
Cu	70	8.0	14	8.0	0.8 - 1.4
Fe	50	60.0	10	60.0	750 - 1500
Hg	10	-	2.0	-	0.5
Mn	10	1.6	2.0	1.6	0.5
Ni	8.0	-	1.6	-	< 0.3
Pb	5	2.5	1.0	2.5	29 - 73 ^e
Sb	-	0.8	-	0.8	-
Se	10	-	2.0	-	0.04 - 0.16
Tl	2.5	-	0.5	-	-
Zn	70	40.0	14	40.0	1000

a - ng per S-Monovette

d - in blood of non-smokers

b - maximum levels of water extractable trace elements^e - in blood in Sweden and

c - provided that 5 mL of blood are collected

China in 1992

Results of the simulated blood collection (using the reconstituted Versieck's 2nd Gen. Biological Reference Material - uncontaminated human serum)) are summarized in Table 3.

Table 3. Chromium and manganese values in reconstituted Versieck's human serum “collected” with SARSTEDT's and BECTON DICKINSON's collection devices for “trace metal (element) analysis”

Sample/Collection device	Cr (µg/L)	Mn (µg/L)
Reconstituted Versieck's serum	< 1.5	1.0
Versieck's mean value (95% CI) ^a [7]	0.069 (0.061-0.079)	0.70 (0.67-0.73)
Monovette®, SARSTEDT	4.4	5.0
Monovette®, SARSTEDT	5.4	3.6
Vacutainer®, BECTON DICKINSON	5.0	4.4
Vacutainer®, BECTON DICKINSON	5.3	4.3

a - dry weight values in ng/g converted to ng/mL of original serum by dividing the former values by 11

Table 3 shows that even higher contamination with chromium and manganese was observed that could be expected from data in Table 2. This clearly demonstrates that the extraneous additions of chromium and manganese from the collection devices exceed several times the element levels in uncontaminated human serum and therefore these devices cannot be used for studying levels of these (and other elements - Cf. Table 2) in human blood and its components. Therefore, our sampling campaign has to be delayed until non-contaminating sampling devices will be obtained.

3.2. Results from previous work relating to this CRP

Exposure to vanadium was studied in occupationally exposed workers of a plant producing vanadium pentoxide from a vanadium rich-slag by a hydrometallurgical process. The production involves several processes that are associated with a release of vanadium-rich dust that presents a risk of occupational exposure, especially if workers do not permanently use their protection respirators.

APM samples were collected mostly at several supervision workplaces of the plant that were considered to be the most significant pollution sources. Hair, nails, blood and urine was collected from both exposed and control persons. The APM, hair, and nail samples were analyzed by INAA, while low level determination of vanadium in blood and urine was performed by a RNAA method with proven accuracy even at the ultratrace vanadium level by analysis of suitable reference materials. Cystine in hair and nails was also measured to elucidate the existing discrepancies about suitability of this test to indicate occupational exposure to vanadium.

Determination of vanadium levels in hair, fingernails, blood and urine in both exposed and non-exposed persons made it possible to evaluate the sensitivity of biological monitoring of exposure to vanadium. This was done in two possible ways: i) by comparing the maximum value of the exposed group to the median of the control group C-2 (criterion 1); ii) by comparing the median of the exposed group to the median of the control group C-2 (criterion 2). These comparisons are presented in Table 4.

Evaluation of sensitivity of the tests studied suggests that the vanadium determination in hair and fingernails might be considered the most sensitive bioindicator of occupational exposure to vanadium. About the same sensitivity of both tests also resulted in significant correlation of vanadium content in both tissues. Owing to the known growth rate of both tissues, these tests should provide information on long-term body burden with vanadium. On the other hand, significance of these tests should not be overestimated, due to the problems with complete removal of external contamination of the tissues. Obviously, by using various cleaning procedures, different results could be obtained and therefore the results of vanadium determination in both fingernails and hair should be interpreted with a caution.

Table 4. Evaluation of sensitivity of biomonitoring tests of exposure to vanadium

Tissue	Criterion 1	Criterion 2
	$\frac{Max_{(exp)}}{x_{(C-2)}}$	$\frac{x_{(exp)}}{x_{(C-2)}}$
Hair	11,278	1167
Fingernails	17,056	553
Blood	3,875	239
Urine	3,594	145

Vanadium levels in blood and urine are undoubtedly more unambiguous and straightforward indicators of occupational exposure to vanadium, although sensitivity of these tests is 3 to 5 times and 2.5 to 8 times lower for the first and second criterion, respectively, compared to the hair and fingernail tests. Due to the quick excretion of vanadium via the kidneys observed in this work and

also by other authors, vanadium determination in urine should be considered as a test of a very recent exposure (sensitivity of this test will decrease with the time elapsed from the end of exposure). On the other hand, vanadium determination in blood appears to be the best indicator of the long-term body burden with vanadium.

It has also been proved that exposure to vanadium has no effect on cystine levels in fingernails, nor in hair.

The determination of vanadium in hair and fingernails yielded the highest sensitivity for detecting occupational exposure, because up to four orders of magnitude higher values were found in the exposed workers compared to controls. However, the interpretation of these tests may be difficult due to known problems with cleaning these tissues prior to analysis to completely remove external contamination (vanadium rich dust from the factory), without influencing the endogenous element content. Moreover, if another cleaning of hair is employed than the IAEA recommended procedure used in this work, somewhat different results and output of the tests may be expected. This problem appears to be even more severe for fingernails.

For these reasons, blood and urinary vanadium levels should be considered the most reliable indicators of occupational exposure to vanadium. These tests exhibited up to one order of magnitude lower sensitivity compared to hair and fingernail analysis. However, the interpretation of these tests appears to be unambiguous and straightforward provided that no contamination occurred on sampling and analysis, because the mechanisms of excretion of the inhaled vanadium via these body fluids seems to be reasonably well established. None of these tests should be valued over the other, because they may be regarded as having a complementary role. Urinary vanadium appears to be the best indicator of very recent exposure, because this parameter increases within few hours after the onset of exposure and also drops quickly after its cessation. The latter is explained by the rapid excretion of vanadium via the kidneys with a half-life between 12 to 18 hours as was found in one exposed worker in the present work. After excretion of the major part of the inhaled vanadium, increased urinary vanadium was still found. However, no time changes of this elevated level could be studied. Our knowledge about the time response of blood vanadium in humans after the start of exposure is still lacking. However, due to known mechanism of slow remobilization of the absorbed vanadium from the bones after several days following the end of exposure, blood vanadium levels may be regarded as the most suitable indicator of the long-term body burden.

The reliable assay of vanadium in these body fluids in occupationally non-exposed persons is a difficult analytical task. Until now, only well elaborated procedures of RNAA, GF-AAS, preferably with preseparation, and high-resolution ICP-MS proved to be capable of accurate vanadium determination. The RNAA method should be considered superior for this purpose. From the analytical point of view, the reliable vanadium determination in urine is somewhat easier to achieve than in blood, because about 3 to 4 times higher element levels in the former fluid of both normal and exposed persons may be expected. This may be a reason why the determination of vanadium in urine might be preferred. If the above mentioned analytical techniques that are best suited for vanadium determination at the ultratrace level in biological samples are not available, it may be proposed that biomonitoring of vanadium exposure by blood and urine analysis is performed in the following way. The elevated vanadium levels can usually be reliably determined by commonly available GF-AAS methods, provided that appropriate quality assurance procedures on sampling and analysis are pursued. Then, the recently published critically evaluated normal vanadium concentrations in human blood, serum and urine [18,19] may be used for a comparison.

More experimental and other details about this work can be found in Ref. [2].

4. PLANS FOR FUTURE WORK

- Validation of the radiochemical neutron activation analysis (RNAA) method developed for low level determination of Cr (Mn) in human serum and urine by analysis of 2nd Generation Biological Reference Material (uncontaminated freeze-dried human serum)

- Collection of the workplace air born particulate matter in a ferro-alloy production plant and its analysis by the validated INAA and PIXE methods
- Contamination-free collection of blood, urine, hair, and nails from a 15-20 member group of occupationally exposed workers in the ferro-alloy production plant and determination of Cr (Mn) in these tissues by the validated RNAA procedures.
- Evaluation and interpretation of the results obtained.

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Institute where research is
being carried out : **Bhabha Atomic Research Centre.**

Chief Scientific Investigator : **Dr. Paul Alunkal Chacko (Dr. Paul, A.C.)**

Starting date of current contract : **15 December, 1996.**

**CHARACTERISATION OF AIRBORNE Ce, Th AND Cd IN WORKPLACE
AND THEIR CO-RELATION WITH THEIR CONCENTRATIONS IN BODY
FLUIDS AND EXCRETA OF OCCUPATIONAL WORKERS USING
NAA, ICP - AES AND XRF.**

A.C. Paul, P.M.B.Pillai and Sujata Radhakrishnan

Health Physics Unit, Environmental Radiological Laboratory (BARC)
Indian Rare Earths LTD, Udyogamandal, Kerala, 683501.

Madhu G. Nair and Pramilla Sawant

Environmental Studies Section, Health Physics Division, BARC,
Mumbai - 400 085.

A.R.Lakshmanan

Health Physics Unit, Nuclear Fuel Complex, Hyderabad-500 762.

B.S.Negi

Environmental Assessment Division, BARC, Mumbai-400 085.

Anil Kumar and Narayani Krishnan

Radiation Safety Systems Division, BARC, Mumbai - 400 085.

ABSTRACT

Airborne Ce, Th and Cd in the occupational settings were studied at the monazite mineral beneficiation and zinc ore concentrate processing using nuclear and related analytical techniques. Air samples were collected using grab and size selective samplers simultaneously. The size selective sampler consisted of 8- stage Anderson cascade impactor with back-up filter. Size characterisation showed that the Mass Median Aerodynamic Diameter (MMAD) of the airborne dust at the monazite mineral beneficiation ranged from 3 to 10 μm . The Activity Median Aerodynamic Diameter (AMAD) for Th and Ce were also in the same range. Over 85% of the airborne dust associated with zinc concentrate ore handling was above 9 μm however: the MMAD at the down stream processing was about 3 μm . Composite air samples were subjected to leaching in simulated lung serum to find the solubility class. The urine samples of occupational workers engaged in mineral beneficiation showed Th levels ranging from 39 to 552 ng l^{-1} with a geometric mean of 186 ng l^{-1} . The results were obtained using Neutron Activation Analysis (NAA). The observed levels of Th in the urine samples were lower than the predicted levels, due to resistance of the mineral to biochemical leaching. In a limited number of urine samples Ce ranged from 312 to 1587 ng l^{-1} with a geometric mean of 700 ng l^{-1} . These values, also determined by NAA, are unique in occupational settings. The Ce to Th ratio in the samples works out to 3.7 as against their ratio of 2.9 in the monazite mineral. The biological levels of Th and Ce observed in occupational settings need refinement on account of the possible environmental contribution due to uptake of these elements in the natural high radiation background areas. Detailed work on characterisation of dust, simulated leaching and analysis of biological samples is in progress in connection with the CRP.

1 INTRODUCTION

Occupational exposure to thorium bearing mineral and compounds involve radiation exposure, both external and internal. While the internal dose due to inhalation form 30 to 70% of the total exposure due to Th and its daughter products, the relative contribution of each depends on the nature of operations [1]. Thorium being long-lived and relatively insoluble its Committed Effective Dose (CED) has to be properly assessed to ensure adequate radiological protection as per the recommendations of the International Commission on Radiological Protection (ICRP)[2]. Assessment of Th in work atmosphere and its relation to the concentrations in body fluids and excreta of occupational workers need to be known accurately in order to verify adequacy of protection measures and estimate the internal dose for radiation protection purpose. Large uncertainty exists in the data bank of Th in body fluids and excreta of occupational workers. While lack of a reliable analytical method to determine Th at low levels (a few tens of nanogram) was the major problem in earlier years, variabilities in the occupational exposures and physico chemical forms of the material handled added significantly to the uncertainty in the bioassay results [1,3]. The values of Th in urine samples of occupationally exposed individuals varied from 50 to 10000 ng reported by various workers [3,4,5,6]. Considerable uncertainty also exists in the metabolic model for Th and some of the reported values do not entirely support its present metabolic model [3, 6]. Dearth of reliable background data on non-occupational exposures to Th within a large spread of natural background radiation also add to the uncertainty in the interpretation of the results obtained from occupational settings. The biokinetics of Th especially its dissolution and clearance from the lung are important in its dosimetry. These aspects are not properly understood in relation to its minerals and compounds.

Health effects due to medical and therapeutic applications of Th compounds have been well documented at higher levels of administration [5,7,8]. Such data are not relevant in occupational settings as the exposures are in low levels. While assay of Th at a few microgram levels can be made fairly accurately by common radiometric techniques using suitable matrix it is difficult and uncertain to measure it at lower levels that exist in biological samples without resorting to sensitive technique such as Neutron Activation Analysis (NAA). Since Th is assuming greater significance in future nuclear energy production programmes work related to its protection assume significance.

Processing of Th from monazite involves separation from Rare-Earth Elements (REE), the most abundant REE being cerium. Much less data exist in respect of Ce in work place. Mausner [9] reported limited study on airborne levels of REE in a Th refinery, using EDXRF. Laboratory studies reported by Palmer[10] showed toxic effects of REE. A few studies reported pathological condition known as 'cerium pneumoconiosis' in occupationally exposed individuals [11,12,13,14]. One such study employed tissue analysis using NAA. Though some authors stressed the need to fix TLV for Ce, limited information obtained from occupational settings did not permit such postulations. There is need to undertake detailed studies on characterisation, uptake and biological transfer of Ce in a systematic manner using reliable and sensitive analytical techniques. Since Ce and Th are in a definite ratio in monazite and -2-many other rare-earth minerals Th could be used as a nuclear analogue to Ce in a limited way. Moreover, NAA offers a unique advantage to estimate Ce and Th simultaneously at levels hitherto unachieved by other analytical techniques.

Work related to cadmium has been documented with respect to the monitoring protocol and biological indices. Biological action levels with respect to concentration in urine/blood have also been suggested[15]. Characterisation of the airborne Cd in line with the approaches adopted for Th and Ce as discussed above may yield valuable new data relevant to occupational and environmental settings.

2 METHOD

The methods which are presently in use and those which are proposed to be used for sample collection, processing, analysis and data evaluation are discussed in this section.

2.1 Sampling and analysis

2.1.1 Airborne particulate matter: Air sampling was undertaken at the mineral beneficiation, monazite processing and zinc smelter plants situated at southern peninsular India.

Grab and size selective sampling devices are employed for atmospheric monitoring of work places. The grab samplers consist of suction pumps of varying capacities ranging from 2.5 to 5 l min⁻¹ for personal samplers and 9 to 60 l min⁻¹ for static samplers. High efficiency (>99%) particulate filters such as GFA, APM 2000 and Millipore are used as the collection media. Choice of the filter paper is based on its suitability for subsequent processing and analysis. Size selective samplers work on the principle of impaction. Half-inch HASL cyclone at 9 l min⁻¹ for gross and respirable sampling and 8-stage Anderson cascade impactor at 28 l min⁻¹ are normally used for this. The former provides information on pulmonary deposition and the latter provides fairly accurate data on the Mass Median Aerodynamic Diameter (MMAD) of the airborne particulates and provides quantitative assay of different size fractions present in the total suspended dust. Some of samplers used are shown in Figure 1.

Detailed sampling protocol using the Anderson cascade impactor is provided in Annex I.

The filter papers are dried at 105°C to constant weight and kept in a desiccator before use. The samplers are operated at the work areas for durations extending up to 1 week depending on the dust concentration and type of samples to be obtained. At the end of sampling, the filters are dried at 105°C to constant weight. The difference in weight is noted and the airborne suspended particulate matter is assessed in the volume of air sampled. From the Anderson samples the aerodynamic particle sizing is carried out from the amount of dust collected on different impaction stages corresponding to the different effective cut-off diameters (ECD). Thereafter, the results are plotted on a log-probability graph with ECD in the ordinate and cumulative % greater than the stated size range by weight in the abscissa. The MMAD is read at 50% probability. The GSD is also determined (see, Annex I). The typical samples obtained at different stages in the Anderson sampler are shown in Figure 2.

The Activity Median Aerodynamic Diameter (AMAD) is determined by nuclear counting. The filter papers are subjected to alpha counting using a ZnS (Ag) scintillator coupled to a photomultiplier and radiation counting system. The counter has low background

(0.1 count min⁻¹) and 30 % efficiency form ²²⁶Ra alphas. The counts obtained are divided by 6 in order to relate it to ²³²Th and are plotted on a log-probability graph. The AMAD and associated GSD are determined.

Leaching studies: The air filter samples obtained are subjected to leaching (for Th and Ce) using lung serum simulant as follows :

The grab samples obtained from a particular process area are pooled together. For this purpose 50 samples collected at different dates covering 3 to 6 months of operation are composited. Two sets of such samples are prepared. These are gamma spectrometrically analysed in a multichannel analyser to determine the ²³²Th content. One set is used to determine Ce by ICP-AES. Samples in the other set are closely packed, one upon the other, inside a perforated perspex can of 4 cm diameter and 6 cm length. The can is kept immersed in simulated lung serum, 1 l of which is taken in a 2 l glass beaker. The beaker is kept in an incubator at 37°C. The set-up used for the leaching studies is shown in Figure 3. (Composition of the simulated lung serum is provided in Annex II.) Aliquots of the leachant is drawn in 100 ml lots at intervals of 1,2,6,10,30,90 and 180 days. Each time the solution is made-up to its original volume by a fresh lot of lung serum simulant. The drawn solutions (100 ml) are filtered through Millipore filter of 0.45 µm pore size. To the filtrate is added 100 mg of Ca as CaCl₂ (1 ml solution), and the solution acidified to a pH 3. Oxalic acid is added to precipitate cal. oxalate. (Cal. Oxalate quantitatively carries with it both Th and Ce). The Cal oxalate precipitate is filtered and the filter paper encapsulated in a double-lined polythene cover. This in turn is placed inside a perforated PVC bottle and irradiated in a research reactor under a neutron flux of 10¹² n cm⁻²s⁻¹. After appropriate cooling the irradiated samples are analysed gamma spectrometrically to estimate Th and Ce. (Detailed methodology for estimation by NAA is provided in Annex III).

Gross air samples collected from different process areas are also composited and subjected to gamma spectrometry and NAA to estimate Th and Ce as per method outlined .

2.1.2 Urine samples: Overnight (16-hr) urine samples are collected by the occupational workers at their residence in a 1.2 l capacity PVC container. The samples brought to the laboratory are acidified with conc. HNO₃ (30 ml for 500 ml) and boiled to destroy the organic matter, after adding 100 mg Ca carrier. The sample is cooled and neutralised by slow addition of ammonia to precipitate cal. phosphate at alkaline pH (10-11). The precipitate is allowed to settle and after decanting out the supernatant the organic matter is completely destroyed by HNO₃-HClO₄. The white precipitate is dissolved in HCl at pH 3. 10 ml saturated oxalic acid is added to precipitate cal. oxalate which is filtered through Millipore/Whatman filters, washed, dried and sealed in polythene covers. Appropriate blank and standard are prepared in similar matrix which accompany every set of samples irradiated and analysed by NAA. 150 urine samples have been collected and processed for the CRP.

2.1.3 Blood samples: 10 to 15 ml blood is sampled from occupational workers after they underwent bath and changing to street clothes. Disposable needles are used and the blood samples are directly collected into PVC centrifuge sample tubes. The serum is separated from sediment. Both fractions are separately dried, homogenised and sealed in polythene covers and subjected to NAA along with appropriate blank and standard. 40 blood samples have been collected and processed for the CRP.

2.2 Quality assurance:

The criteria is applied to pre-analytical (sampling) and analytical stages. While adequate number of samples are ensured for meaningful interpretation of results, care is exercised to keep the samples free from contamination by extraneous sources during collection and processing. Every set of sample is accompanied by a blank at every stage of its processing. Use of demineralised double-distilled water and analytical grade reagents make it possible to achieve low background levels approaching the sensitivity of the technique employed (5 ng for Th and 10 ng for Ce). Matrix specific standards matching the expected concentration levels are prepared and accompany every set of sample undergoing irradiation, cooling and nuclear counting. The secondary standards are prepared by appropriate dilution of the primary standards which is subjected to periodic calibration by at least two different techniques. For nuclear counting use of low background counters and overnight counting reduce the error to acceptable levels.

3 RESULTS

3.1 Review of earlier work relating to the CRP

The airborne particulates associated with the beach mineral mining and mineral separation plants were studied and reported [16]. These studies employed 8-stage Anderson cascade impactor for physical characterisation of the gross dust in terms of the MMAD. The studies reported that approx. 75% of the airborne dust had MMAD greater than 11 μm at the mineral separation plants and that fraction was considered non-respirable. The remaining fraction, < 11 μm (approx. 25% of the total dust), had an MMAD of 4.5 μm with a GSD of 1.8. Limited studies reported on leachability assigned solubility class Y for the mineral dust. The studies indicated scope for future work in characterisation of dust, detailed leachability experiments employing sensitive techniques at low-levels and correlation of occupational exposure with levels observed in biological samples. In a related study on biological monitoring conducted on a limited group of occupational workers a correlation was reported for Th between the air samples from the chemical processing plant and urine samples of the occupational workers, however no such correlation was apparent at the mineral separation plant [4].

3.2 Work carried out under the CRP

The work is presented under three broad divisions as follows:

- Physical characterisation of airborne particulates (Th, Ce and Cd)
- Chemical solubilisation studies (Th & Ce)
- Determination of Th and Ce in urine samples of mineral beneficiation workers by NAA.

3.2.1 Physical characterisation of the airborne particulates:

Figure 2 is a pictorial presentation of a typical dust sample collected at different impactor stages of the Anderson sampler. Tables I and II present the distribution of the total

airborne dust as a function of the particle size at the mineral beneficiation process. Table I, detailing the conditions prevailing at the processing areas involving coarse handling techniques such as drying, screening, high tension separation and tabling shows MMAD of 10 μm with GSD of 3. In a major deviation from the earlier reported work all the dust collected was used to arrive at the MMAD which resulted in the new value. Data in Table II representing general areas show distinctly lower MMAD in the range of 3 to 5 μm and represents conditions at which particles of higher MMAD have depleted from the atmosphere due to fast settling. Incidentally, this figure agrees well with the value of 4 obtained in the earlier study.

In the operations involving Th, it is necessary to derive the Activity Median Aerodynamic Diameter (AMAD) in order to arrive at the Derived Air Concentration (DAC), Pulmonary Deposition (PD), etc. Determination of AMAD involves a simple nuclear technique of gross activity counting and can be employed for matrices having low specific activity especially in occupational settings involving mining, mineral beneficiation and metal purification such as in thorium and uranium industries. Analysis of the airborne dust for particle size for the mineral beneficiation process gives values ranging from 3 to 11 μm as AMAD for ^{232}Th with GSD in the range of 3 to 5 (Table III). Since Ce to Th bear a constant ratio of 2.9 in monazite by weight the MMAD of Ce has been indirectly estimated to be the same as that of ^{232}Th as observed above. The study has not shown any substantial difference in values between AMAD and MMAD indicating that the activity is volume distributed.

Table IV and Table V provide data on similar studies conducted at a zinc smelter unit purifying Cd by electrolytic process. Table IV provides distribution of airborne dust at the initial ore processing such as powdering and roasting. Nearly 85% of the dust is in the stage corresponding to ECD of 9 μm . Estimation of MMAD taking this fraction results in a high value of about 100 μm . However, when this fraction is eliminated the remaining fraction of the airborne dust gives an MMAD of 12 μm with a GSD of 3.0. The situation changes at the downstream end (electrolysis) where the airborne dust is distributed in substantially lower sizes and the MMAD works out to about 3 (Table V). A significant fraction (approx. 10%) of the total dust collected from this process ends up at the back-up filter which collects particles of less than 0.4 μm .

The smallest weight of the sample collected was 0.02 mg. The error in weighing this amount is 50 % (sensitivity 0.01 mg). For nuclear counting the method has 20% error at 1 σ confidence level. However, gravimetric or gross counting methods cannot be effectively employed in outdoor sampling where low dust-loading imposes severe limitation in its assay. Nuclear methods such as NAA which offer higher sensitivity have to be employed in such situations.

3.2.2 Solubilisation studies (Th & Ce):

Four sets of samples from the chemical processing plant presently undergo leaching studies employing simulated lung-serum including a reagent blank. A total of 30 samples have so far been collected over a period of 3 months. All the samples have been processed up to the stage of NAA. (Results of these samples will be presented later.)

3.2.3 Determination of Th and Ce in urine samples of mineral beneficiation workers using NAA:

Table VI provide the results of urine sample analyses for Th with respect to 34 occupational workers. Twelve of these samples have also been analysed for Ce. The concentration of Th vary from 39 to 552 ng l⁻¹ showing a geometric mean of 186 ng l⁻¹. The observed concentrations vary by a factor of 15. Variations of a higher order in urine have been reported earlier[3]. The observed urinary concentrations have to be viewed in the light of the ICRP Reference Man data[17] which provides a derived concentration of 70 ng l⁻¹ as the background. Many of the subjects under investigation reside at the natural high background radiation areas. Exposure to higher levels of airborne Th at these areas has been reported[18]. Higher levels of Th in urine have also been observed in a limited study conducted earlier[19]. Therefore, it is necessary to establish site specific background of the population for co-relating the findings with occupational exposure and the individual results merit case by case analysis.

The data on Ce levels in the Table are unique as similar results are not reported in occupational settings. The concentrations of Ce vary from 312 to 1587 ng l⁻¹ of urine with a geometric mean of 700 ng l⁻¹. Variation observed is in a narrow range, by a factor of 5. Significant concentration due to uptake from natural high background sources is expected, similar to that for Th and hence the values have to be qualified further. The ratio of the mean concentrations of Ce and Th show a value of 3.3 for arithmetic mean and 3.7 for geometric mean. These ratios are to be viewed in the light of the ratio of Ce to Th in monazite which is 2.9. Detailed studies are in progress to fully understand this in terms of biokinetics.

4 PLANS FOR FUTURE WORK

Future plans envisaged to be completed next year are listed below:

- Detailed elemental (Th, Ce & Cd) characterisation of the airborne particulates.
- Leaching studies employing lung-serum simulant and digestive fluid for (Th, Ce & Cd).
- Co-relation of the airborne elemental levels (Th, Ce & Cd) with blood and urine excreta of occupational workers.
- Co-relation between Th in urine, blood and exhaled breath.
- Establishing site specific background levels.

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- * Publications related to the CRP

Table I

**PARTICLE SIZE ANALYSIS OF AIRBORNE DUST FOR
MINERAL BENEFICIATION (PROCESS AREAS).**

Sample code : MKIASA

Stage No.	Effective cut-off dia (μm)	% weight at stages			
		1	2	3	4
0	9.0	58.6	55.0	56.6	51.5
1	5.8	14.2	19.0	14.3	14.9
2	4.7	6.4	6.8	4.9	8.4
3	3.3	10.1	6.8	6.1	9.2
4	2.1	9.3	7.0	8.9	7.5
5	1.1	0.4	4.7	8.2	5.0
6	0.7	0.7	0.5	0.8	0.1
7	0.4	<0.1	0.2	0.1	1.7
8	<0.4	0.3	<0.1	0.1	1.7
MMAD (μm)		11.0	9.8	9.1	12.5
GSD (σ g)		2.8	2.6	2.3	4.5

No. of samples - 6

No. of stages - 54

Table II**PARTICLE SIZE ANALYSIS OF AIRBORNE DUST FOR
MINERAL BENEFICIATION (PROCESS AREAS).**

Sample code : MK2ASA

Stage No.	Effective cut-off dia (μm)	% weight at stages	
		1	2
0	9.0	24.7	11.3
1	5.8	19.6	7.3
2	4.7	15.9	10.7
3	3.3	12.4	13.9
4	2.1	3.1	20.4
5	1.1	7.5	14.7
6	0.7	4.2	6.2
7	0.4	6.2	3.0
8	<0.4	6.4	12.5
MMAD (μm)		5.2	2.6
GSD (σ g)		4.0	3.2

No. of samples - 2

No. of stages - 19

Table III

**PARTICLE SIZE ANALYSIS OF Th (Ce) FOR MINERAL
BENEFICIATION BY NUCLEAR COUNTING**

Sample code : MK ASA

Stage No.	Effective cut-off dia (μm)	% activity at stages			
		Process areas		General areas	
		1	2	1	2
0	9.0	45.3	31.4	12.3	14.8
1	5.8	18.7	17.4	17.8	10.8
2	4.7	9.1	13.3	23.5	12.9
3	3.3	9.1	15.2	15.3	3.1
4	2.1	7.0	10.9	9.2	14.8
5	1.1	3.4	6.5	4.1	17.1
6	0.7	2.9	2.5	8.4	13.1
7	0.4	2.6	1.6	7.4	10.1
8	<0.4	1.9	1.2	2.0	3.3
AMAD (μm)		11.0	6.6	4.8	2.7
GSD (σ g)		4.6	3.2	3.7	4.2

No. of samples - 8

No. of stages - 72

Table IV

**PARTICLE SIZE ANALYSIS OF AIRBORNE DUST FOR
ZINC SMELTING - (INITIAL PROCESS AREAS).**

Sample code : BZIASA

Stage No.	Effective cut-off dia (µm)	% weight at stages		
		1	2	3
0	9.0	91.6	78.4	82.1
1	5.8	5.0	9.5	8.9
2	4.7	1.5	3.2	2.4
3	3.3	1.1	2.5	2.1
4	2.1	0.5	1.9	1.7
5	1.1	0.3	1.1	0.5
6	0.7	0.06	1.5	0.6
7	0.4	0.04	0.5	0.6
8	<0.4	<0.01	1.4	1.1

No. of samples - 3

No. of stages - 27

Table V

**PARTICLE SIZE ANALYSIS OF AIRBORNE DUST FOR
ZINC SMELTING (ELECTROLYSIS PROCESS).**

Sample code : BZ2ASA

Stage No.	Effective cut-off dia (μm)	% weight at stages	
		1	2
0	9.0	32.5	10.1
1	5.8	2.4	3.9
2	4.7	8.7	16.4
3	3.3	16.7	10.2
4	2.1	9.5	13.3
5	1.1	7.1	15.6
6	0.7	2.4	9.4
7	0.4	7.2	9.4
8	<0.4	13.5	11.7
MMAD (μm)		3.6	2.2
GSD (σ g)		5.0	3.6

No. of samples - 2

No. of stages - 18

Table VI**CONCENTRATION OF Th AND Ce in URINE SAMPLES OF
OCCUPATIONAL WORKERS****(MINERAL BENEFICIATION)**

Employee Code	Concentration in urine (ngl ⁻¹)	
	Th	Ce
M 1	85	--
M 2	291	--
M 3	134	--
M 4	255	--
M 5	44	--
M 6	50	--
M 7	181	--
M 8	141	--
M 9	104	--
M 10	354	--
M 11	130	--
M 12	234	--
M 13	88	--
M 14	101	--
M 15	552	--
M 16	39	--
M 17	500	--
M 18	544	--
M 19	234	--
M 20	278	--
M 21	165	--
M 22	177	--
M 23	373	1280
M 24	224	757
M 25	132	535
M 26	450	1459
M 27	96	516
M 28	96	422
M 29	407	1587
M 30	94	441
M 31	530	779
M 32	370	731
M 33	244	312
M 34	318	678

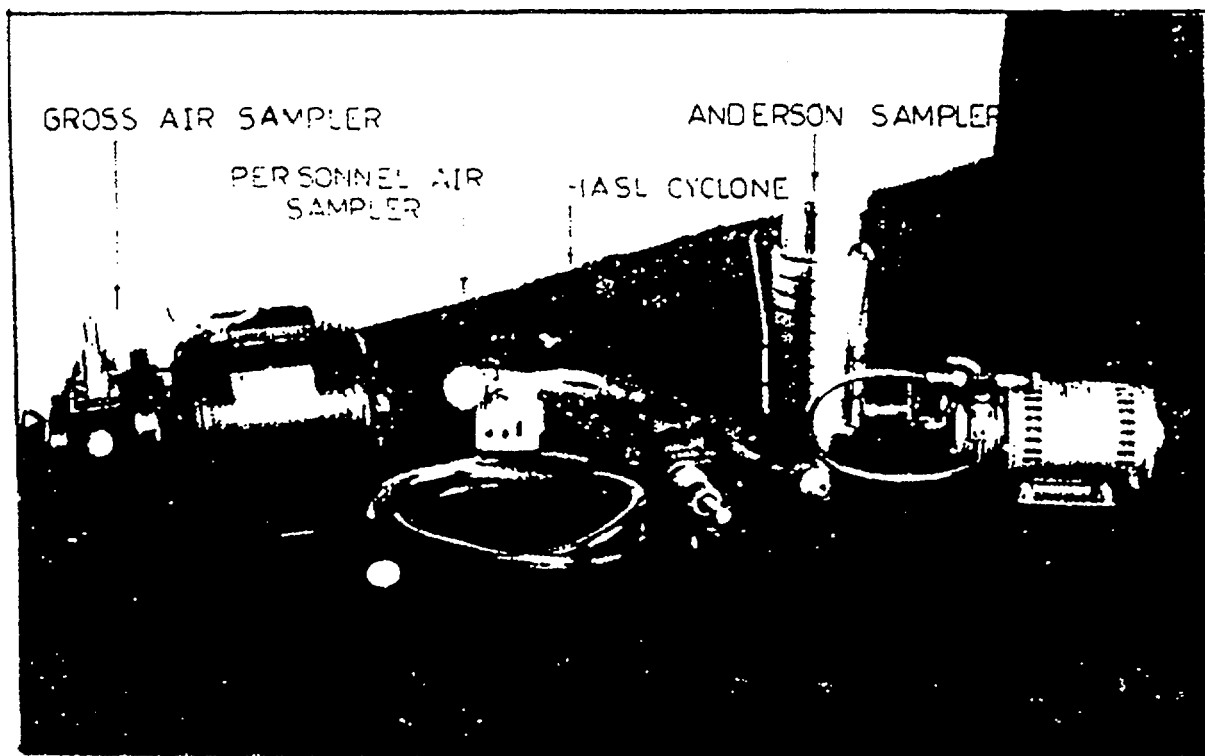


FIG:1. AIR SAMPLERS

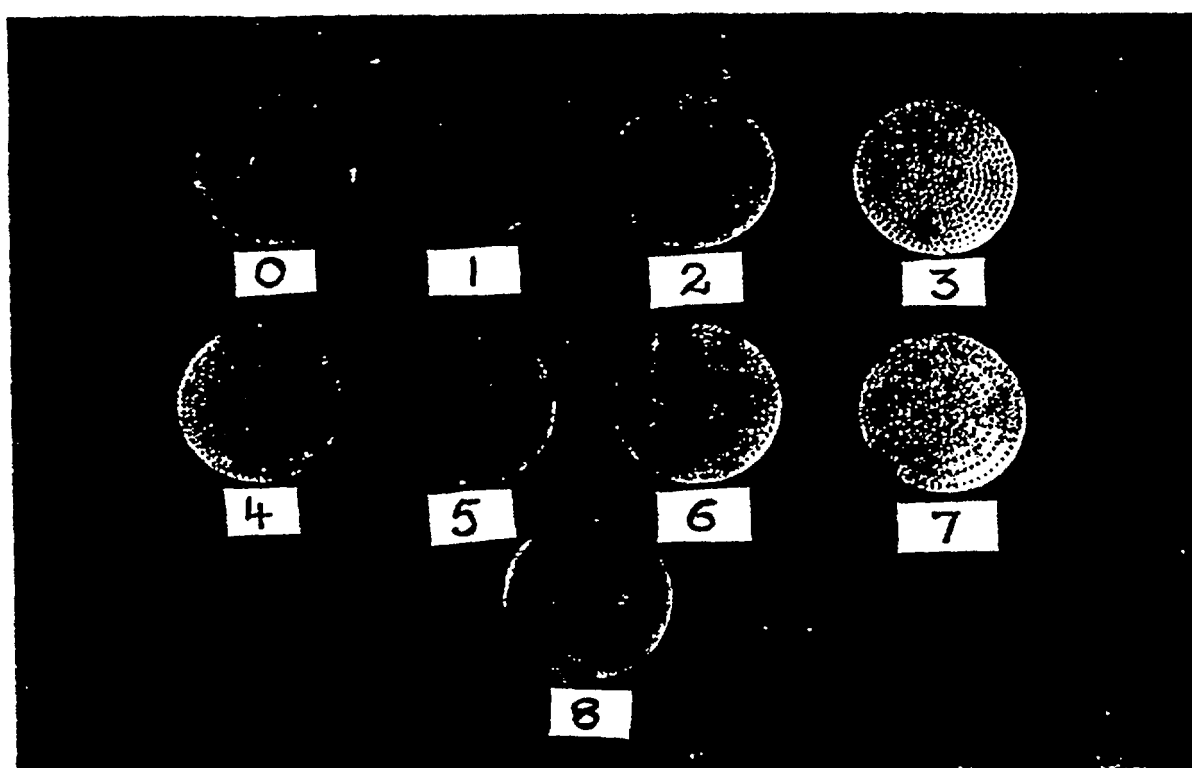


FIG. 2. SAMPLES COLLECTED ON DIFFERENT STAGES
IN ANDERSON SAMPLER

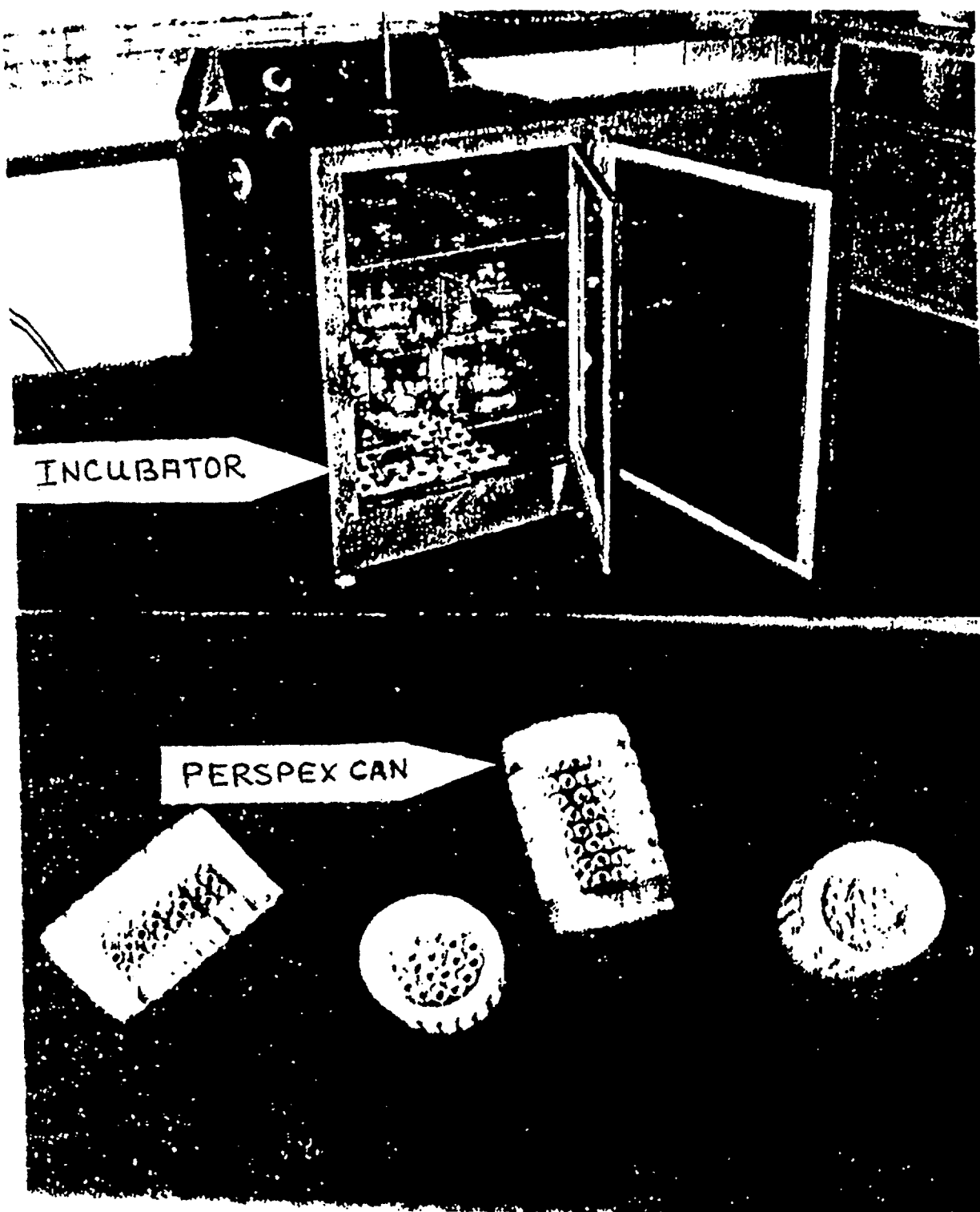


FIG. 3. EXPERIMENTAL SETUP FOR LEACHING STUDIES

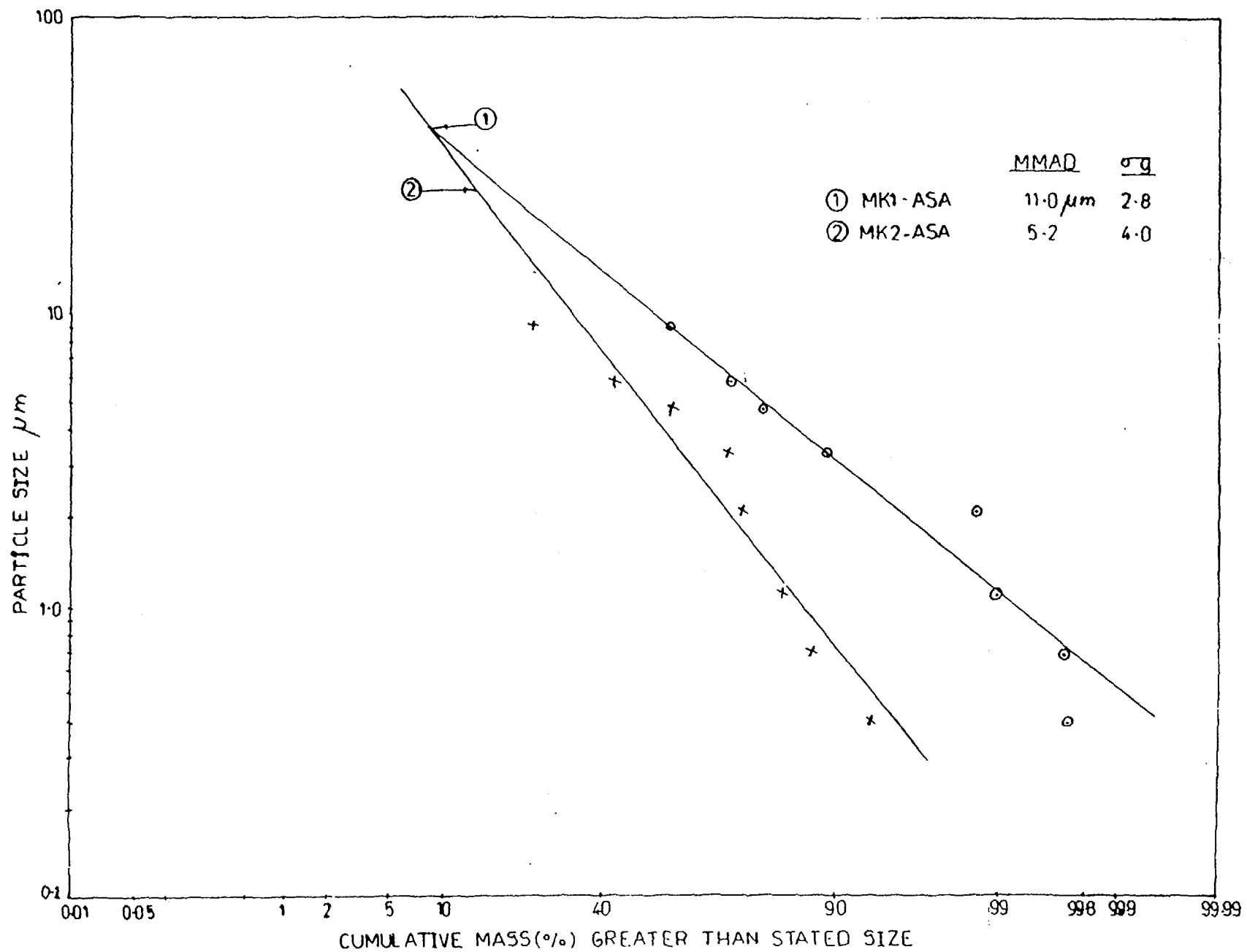


FIG. 4 PARTICLE SIZE DISTRIBUTION OF AIRBORNE DUST IN MINERAL BENEFICIATION PROCESS

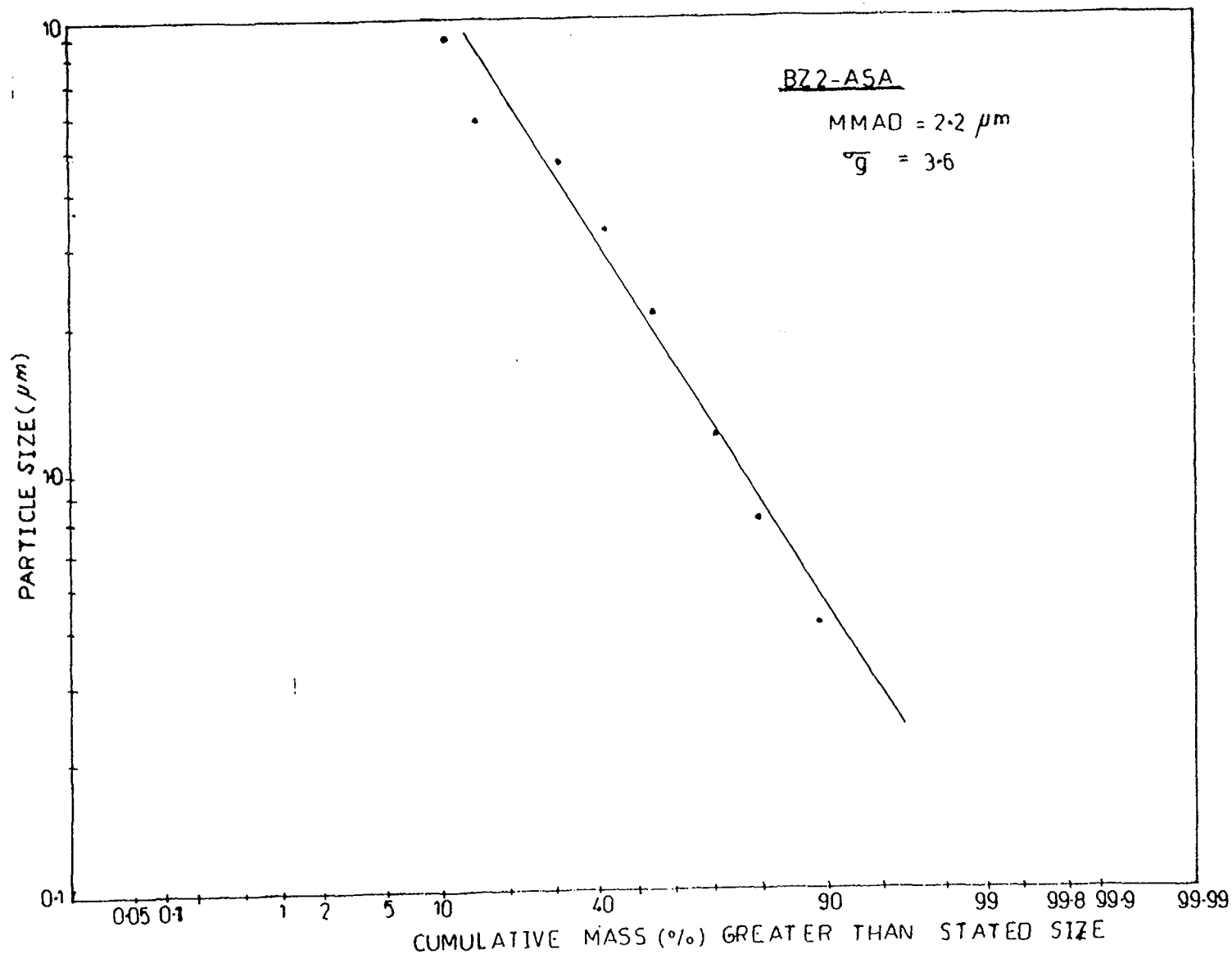


FIG. 5 PARTICLE SIZE DISTRIBUTION OF AIRBORNE DUST IN ZINC SMELTING PROCESS

Annex I

Aerodynamic particle sizing

The human respiratory tract is an aerodynamic classifying system for airborne particulates. The respiratory tract regions defined in the new ICRP model is provided in Figure A 1. Any sampling device used should reproduce to a reasonable degree the dust collecting characteristics of the human respiratory system. The sampling device should classify the particles according to the aerodynamic dimension which is a true measure of lung penetrability. The fraction of inhaled dust retained in the respiratory system and the site of deposition vary with size, shape, density and solubility of the particle. Methods that employ light scattering or filtration and microscopic sizing of particles do not reckon with density and some other properties that affect the movement of particles in air.

The collection of a particle by an obstacle is a function of the inertial impaction parameter:

$$K = \frac{C_p U D^2}{18 \mu D_c}$$

where U is the relative velocity, p is the particle density, D is the particle diameter, μ is the gas viscosity, D_c is the diameter of the round jet and C is the Cunningham slip correction factor.

Data from inertial impactor are normally presented as 50% effective cut-off diameters. For Anderson impactors (having round jets and flat collection surfaces, the 50% effective cut-off would give a value of 0.14 for the inertial impaction parameter (K). The Cunningham slip factor corrects for the fact that as particle diameters approach the mean free path length of the gas molecules they tend to slip between the gas molecules and are more easily able to cross the bulk flow streamlines. The collection efficiency will be slightly greater than that of inertial impaction for particle diameter of 1 to 2 micrometer.

Anderson Ambient Particle Size Samplers

This is a multistage, multiorifice cascade impactor to measure size distribution and total concentration of particulate matter. The sampler is calibrated with unit density (1 g cm^{-3}) spherical particles regardless of their physical size, shape or density. The aerodynamic dimensions obtained can be used to determine the probable point of respiratory deposition and the particle behaviour in the atmosphere. The data obtained can also be used to examine compliance with the TLV values and help in the design of proper air sampling and air cleaning devices.

Description

The Anderson 1 cfm Ambient Air Sampler is comprised of 8 stages. Each impactor stage contains multiple drilled orifices. When air is drawn through the sampler, the jets of air at each stage direct the particles towards the collection surfaces of the respective stage. The size of jet becomes smaller for succeeding stages. Impaction of the particle at any stage depends on its aerodynamic dimension.

Particles that are not collected on the first stage follow the air stream around the edge of the plate to the next stage, when it is either impacted or passed on to the succeeding stage. The orifices are progressively smaller from top to bottom stages, ranging from 0.1004" dia (0.221 cm) to 0.01" dia (0.025 cm) on stage 7. Each stage has a removable stainless steel (3.25" dia.) collection plate. The exhaust section of each stage is approx. 0.75 " larger than the collection plate allowing unimpacted particles to go around the plate and to the next stage.

For sampling atmosphere containing particles larger than 10 μm pre separator can be used to prevent particle bouncing and reentrainment errors.

Operation of the equipment (Sampling)

Orifice stages, pre separator and collection plates must be clean. A mild detergent with warm water is usually sufficient for cleaning. The stages are numbered 0, 1, 2, 3, 4, 5, 6, 7 and 8. Stage 0 is an orifice stage only. Stage 8 contains the collection plate for stage 7 followed by a back-up filter. Each stage has an O-ring for sealing. The collection substrates consist of glass fibre or cellulose devices. These are to be pre-conditioned and pre-weighed before loading.

Fig.A2 shows how impaction occurs at orifice collector interfaces. Particle size range collected at each stage depends on the orifice velocity of the specific stage, distance between orifices and collection surface and the collection characteristics of the preceding stage. The constant flow rate and successively decreasing orifice diameters resulting in increasing velocities result in impaction of progressively smaller particles in succeeding stages. At 1 cfm flow the fractionation ranges from 10.0 to 0.4 micrometers. The particles that are too small to be impacted are collected in the backup filter. The sampling time may vary from few minutes to several hours. Re-entrainment may occur at loadings above 10 mg at any stage and hence the stages should be inspected occasionally.

After sampling, the set up is disassembled and the collection media are conditioned prior to weighing in a desiccator (airborne- particulates have hygroscopic properties). Weighing should have an accuracy of $\pm 0.02\text{mg}$ with a precision of 0.01mg.

Data analysis

Normally stainless steel or glass is not used as the collection surface due to high tare weight to sample weight ratio. (However these can be used if the analysis requires washing of the collected material.) The following steps are involved in the assay of particle size after completion of sampling.

- a) Determine the weight of sample collected at each stage including the back-up filter. Add all the weights and find the total weight of the sample.
- b) Divide the weight collected at each stage with the total weight of the sample to get the percentage of the total at each stage. (The particle density should be considered as 1.0 g cm^{-3} so that particle sizes can be reported as equivalent aerodynamic diameters.)
- c) Obtain the Effective Cut-off Diameters (ECD) as follows:

Stage No. -----	ECD (μm) -----
0	9.0
1	5.8
2	4.7
3	3.3
4	2.1
5	1.1
6	0.7
7	0.4
8 (back-up filter)	< 0.4

- d) The results should be plotted in log-probability graph with ECD in the ordinate and the cumulative % greater than the stated size range by weight in the abscissa. Find the median size at 50% probability.

- e) The geometric standard deviation is given by

$$\sigma_g = \frac{50\% \text{ diameter}}{84.13\% \text{ diameter}} = \frac{15.87\% \text{ diameter}}{50\% \text{ diameter}}$$

Generally the particle size information should be presented in graphical form with the mass median diameter and the geometric standard deviation.

Annex II

Composition of Lung Serum Simulant Solution*

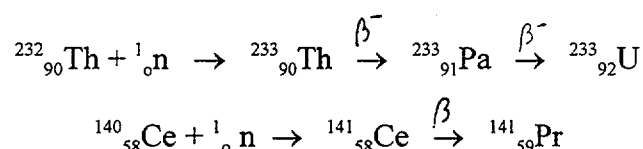
Chemical Species	composition (m mol per litre)
Sodium	145
Potassium	traces
Calcium	0.2
Magnesium	traces
Ammonium	10
Protein	traces
Chloride	126
Bicarbonate	27
Phosphate	1.2
Citrate	0.2
Organic acid	6
Sulphate	0.5

* Source: Kanapilli,G.N; Goh, C.H.T and Chimneti, R.A. Measurement of In-Vitro Dissolution of Aerosol Particles for Comparison to In-Vivo Dissolution in the Lower Respiratory Tract after Inhalation. Health Physics.24 (1973) 495-507.

Annex III

DETAILED PROCEDURE FOR ESTIMATION OF Th AND Ce BY NAA

The precipitate along with the filter paper is sealed in a polythene cover. ^{232}Th standard and Ce standard are prepared in similar matrix and sealed in polythene covers. A set of 4-5 samples along with Th and Ce standards are sealed together in another polythene cover. This packet is double sealed and placed in a perforated PVC container. The container is immersed in the moderator(water) of a 'swimming pool' type of research reactor in a neutron flux of $10^{12} \text{ n cm}^{-2}\text{s}^{-1}$. The irradiated sample is allowed to cool for 5 days for the decay of short-lived activation products. Thorium is determined by counting the 311.8 KeV gamma of ^{233}Pa . Cerium is determined by counting the 145.4 KeV gamma of ^{141}Ce . The nuclear reaction leading to the formation of ^{233}Pa and ^{141}Ce are as follows:



The gamma spectrometric assay is carried out using a 54 cm³ HPGe detector coupled to 1024 channel analyser. The amount of Th and Ce present in the sample is determined by comparison of the activities in the sample and the standard as follows:

$$\frac{\text{As}}{\text{Astd}} = \frac{\text{Ws}}{\text{Wstd}}$$

where	As	=	Activity in sample
	Astd	=	Activity in standard
	Ws	=	Weight of Sample
	Wstd	=	Weight of standard.

Appropriate decay correction for the sample and standard, are applied.

Note 1

Neutron Activation Analysis (theoretical aspect) :

A sample is irradiated in a flux of neutrons in a nuclear reactor. The isotopes of the various elements absorb neutrons. Many of these reactions give rise to radioactive products, the activity of which is measured.

The activity , A, is given by

$$A = N \phi \sigma \theta (1 - e^{-\lambda t})$$

where N = number of atoms of the element in the sample.

ϕ = neutron flux ($n \text{ cm}^{-2}\text{s}^{-1}$)
 σ = neutron capture cross section of the target nuclide.
 θ = fractional isotopic abundance of the target nuclide.
 λ = decay constant of the product nuclide
 t = duration of irradiation.

Note 2

Nuclear data for neutron activation of Ce and Th

	Ce	Th
Mass no.	40	232
Atomic No.	58	90
Isotopic abundance (%)	88.48	100
Activation cross suction(b)	0.57	7.4
Daughter nuclide	$^{141}_{58}\text{Ce}$	$^{233}_{91}\text{Pa}$
Half-life (d)	33	27.4
Gamma energy (KeV)	145.4	311.8
Gamma abundance(%)	48	44

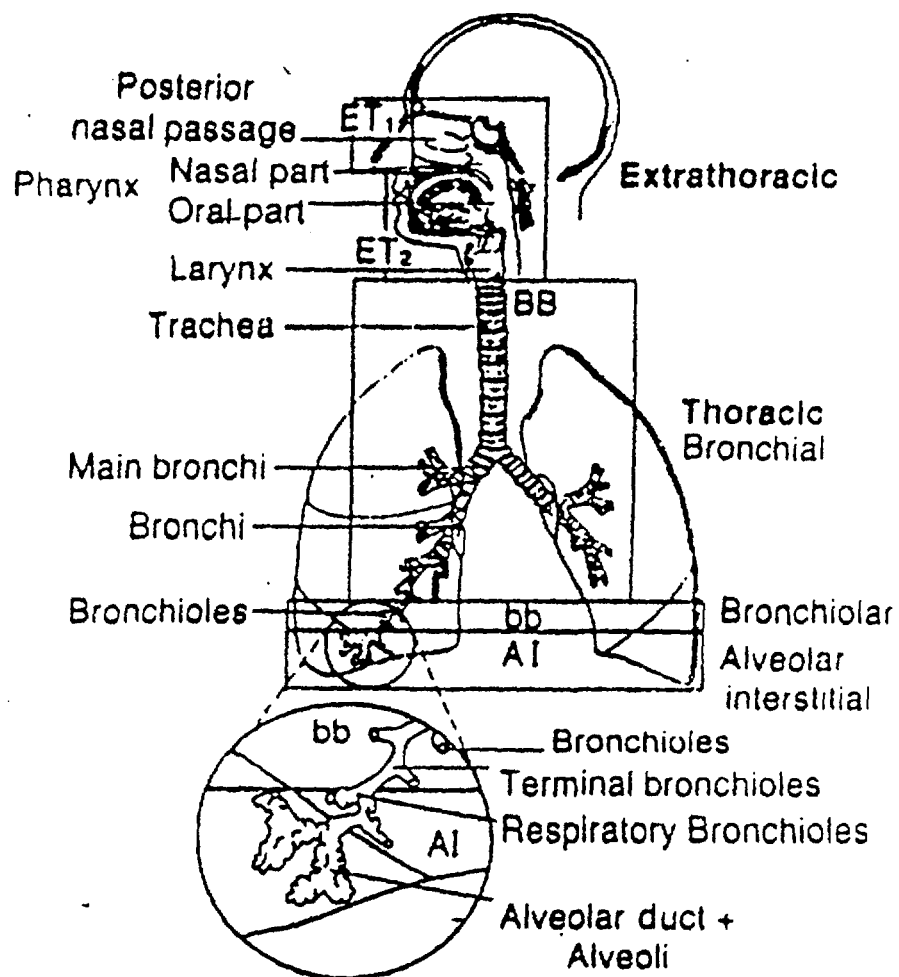


Figure A1. Respiratory tract regions defined in the new ICRP model.

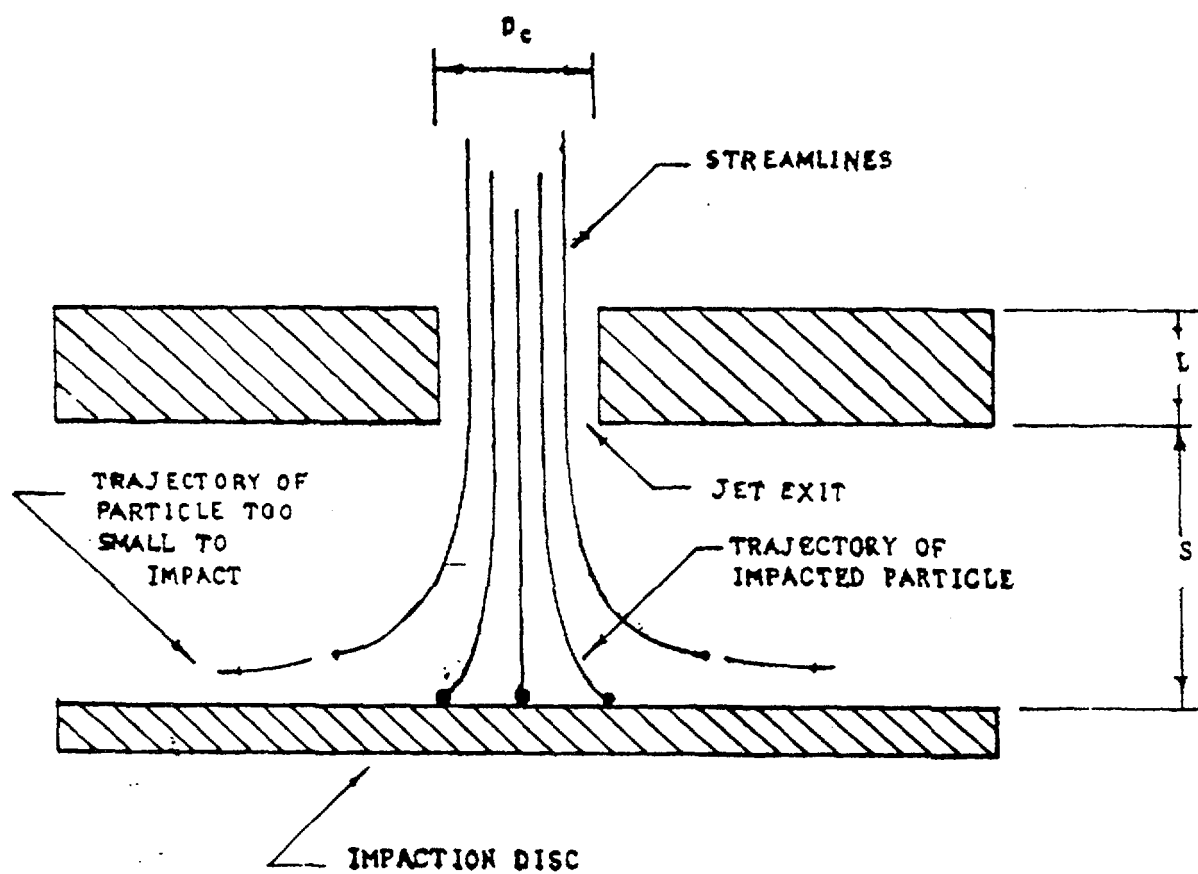


FIG:A2 SCHEMATIC OF IMPACTOR STAGE



XA9950304

Contract Number: 9477/RO/Regular Budget Fund

Title of Project: The use of nuclear and related techniques for the studies of airborne particulate matter in workplace including tissue analysis and possible impacts on human health in a metal industry

Institute where research is being carried out:
National Atomic Energy Agency, Center for Nuclear Technique Research

Chief Scientific Investigator: Dr. Benjamin Widjajakusuma

Starting date of current contract: January 1997

THE USE OF NUCLEAR AND RELATED TECHNIQUES FOR THE STUDIES OF AIRBORNE PARTICULATE MATTER IN WORKPLACE INCLUDING TISSUE ANALYSIS AND POSSIBLE IMPACTS ON HUMAN HEALTH IN A METAL INDUSTRY

Benjamin Widjajakusuma^{*)}, Harjoto Djojosebroto^{**)} and Endang Kumolowati^{**)}

^{*)}Department of Internal Medicine, Medical Faculty University of Padjadjaran, and

^{**)}National Atomic Energy Agency, Center for Nuclear Technique Research

ABSTRACT

Various processes in a metal industry may produce gases and fine airborne particulate matter that hazardous to human health. The present study deals with assessment of levels and health effects of airborne particulate matter in a metal industry. The objective is achieved by determination of elemental levels in blood, nail and hair of workers and airborne particulate matter that are collected from their workplace. The elemental levels in blood, nail and hair of the workers will be compared to those of control. Their health condition are examined by medical examination and biochemical analysis of their blood. The blood was drawn following an overnight fast before breakfast, by means of I.V. catheter into three polyethylene tubes. The blood samples in the first tubes were sent to clinical laboratory for biochemical examination. Those in the second and third tubes, which are considered free from metal contamination by the needle of the catheter, are used for trace element study. Sera in the polyethylene tubes were separated from erythrocyte by centrifugation, then cooled by liquid nitrogen and freeze dried. Approximately 1 g of toe nail and hair samples were taken respectively from every worker. To eliminate grease and surface contamination the hair samples were rinse with acetone. Airborne particulate samples were collected from the workplace using Gent sampler. These samples are ready for elemental analysis. Results of biochemical analysis and medical examinations of the workers are presented in this report. The correlation among various parameters will be determined by statistical analysis.

SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

During the last twenty five years industrialization in Indonesia has strongly support national economic development, and hence improves the quality of life the Indonesian people. The industrial and economic developments, however, are also accompanied by side effects. Various processes in an industry may produce gases and fine airborne particulate matters. Emission of these matters to open atmosphere may cause degradation of environmental quality. Elements in the fine particulate matter may enter human body through inhalation and direct contact with skin. Those elements will be accumulated in the organs, namely liver, kidneys and brain, manifest in clinical syndromes such as hypertension, renal failure and neurological symptoms and signs. The elements are excreted through urinary tract as urine. They can also be excreted through hair and nails. These elements can either have deleterious effects on or considered essential for human health. Selenium for example, is considered essential, as depletion results in a deficiency syndrome and repletion reverses the abnormality. It was observed for example serum se-

lenium level of female acute myocardial infarction is significantly lower than that of normal person. From this observations, by odd ratio, it was shown that the probability of getting myocardial infarction for selenium deficient female was five times higher than that of normal person [1]. Although some elements are considered essential, if present at levels exceeding the limit of safe exposure, they are potentially toxic and therefore hazardous to human health. Microgram amount of selenium in food (40-100 µg/kg of food) is essential, but at higher levels selenium (greater than 1 mg/kg of food) is toxic [2]. Consequently higher level of a certain elements in human tissue (such as blood, hair and nail) than the normal level may indicate intoxication that have deleterious effects on human health.

The present study, the levels and health effects on airborne particulate matter in the workplace is assessed by elemental quantification of blood, nail and hair of workers in a metal industry and airborne particulate samples that are collected at the workplace. The elemental levels in blood, nail and hair of the workers will be compared to those of control which consist of healthy individuals from different places. Their health condition are examined by medical examination and biochemical analysis of their blood. The correlation among various parameters will be determined by statistical analysis.

METHODS

Blood, hair and nail samples are collected from 58 workers of a metal industry in Bandung (about 180 km south east Jakarta). The age of the workers are ranged between 25 - 52 years, and most of them have worked for more than 5 years. They work in several sections, namely smelter, electroplating, heat treatment and painting. In this study they are subject to medical examination, which consist of:

1. Medical history: including family history; symptoms of skin diseases; cardiovascular disorder: palpitation, chest pain, fainting sensation; lung disorder: shortness of breath, chronic cough; neurological symptom such as paresthesia, muscle pain, muscle cramp, seizures, twitching or convulsion; gastrointestinal disturbances: nausea, vomiting; hypertension and infertility. Smoking habit (common or clove cigarettes, total of cigarettes consumed daily), constituents of daily meals and the use copper or aluminum equipment for cooking or boiling water; any diseases or abnormalities observed by the individuals during his working period in the section.
2. Physical examination: routine complete check, resting electrocardiograph: 12 lead ECG.
3. Routine blood check: hematology: hemoglobin; white blood cells; erythrocyte sedimentation rate; packed cell volume; kidney function test: blood urea-N; liver function tests: serum glutamic oxalo-acetate transaminase (SGOT), serum glutamic pyruvate transaminase (SGPT); lipid profile: total cholesterol, high density lipoprotein (HDL) cholesterol, low density lipoprotein (LDL) cholesterol and triglyceride; uric acid.

The preparation of blood sample was performed as follows. The blood was drawn following an overnight fast before breakfast, by means of I.V. catheter Becton-Dickenson USA from cubiti vein with a slight pressure to prevent from hemolysis. Three fractions consist of respectively 10 cm³ blood will freely flow into 3 pre cleaned polyethylene tubes (Sarstedt Germany). The cleaning of the polyethylene tube involving soaking the tube for 3 days in a 15:10:75 (v:v:v) mixture of 65% Suprapur nitric acid, 96% Suprapur Sulphuric acid and quartz-bidistilled water, followed by rinsing with

quartz-bidistilled water and drying the tubes in clean room (room 100). These tubes are stored in a polyethylene bag until use [3].

The blood samples in the first tubes were sent to clinical laboratory for biochemical examination. Those in the second and third tubes, which are considered free from metal contamination by the needle of the catheter, are used for trace element study. To minimize contamination by dust particulate during sample preparation, the following steps were performed in a clean room (room 100). Sera in the polyethylene tubes were separated from erythrocyte by centrifugation twice at 3000 rpm for 20 minutes. In this respect the metal part of the centrifuge is coated with polystyrene. To avoid fractionation during cooling, sera and erythrocyte fraction were then frozen by dipping in liquid nitrogen, and be kept in frozen condition in a freezer at - 40° C. The sera and erythrocyte in the polyethylene tubes were dried using freeze drying equipment (Christ Loc-1).

Approximately 1 g of toe nail and hair samples were taken respectively from every worker. The nail was cut using commercially available stainless steel nail cutter. The hair samples were taken from hair on the back of the head close to the nape. About 2 cm of hair were cut as close to the scalp as possible. To eliminate grease and surface contamination the hair samples were rinse with acetone [4].

Airborne particulate samples are collected from halls or buildings where the workers perform their work. The sample collection were carried out during working hours (from 9 am to 4 pm). The airborne particulate matter were deposited on pre-weighed Nuclepore filters using Gent sampler. Prior to weighing until constant weight the filter paper was equilibrated in a preconditioned chamber at 25° C, 50% relative humidity. The amount of deposited airborne particulate on the filter was determined by weight difference of the filter before and after sample collection.

RESULTS

Fifty eight workers had completed their medical check up, blood test and ECG tracing. Toe nails and hair were stored in small plastic tube.

On physical examinations it was observed that: 34 workers had no abnormality; 2 hypertension (high blood pressure): 1 without abnormality in ECG, 1 had left ventricular hypertrophy & myocardial ischemia); 7 hypotension (low blood pressure) with normal ECG; 2 hypotension with suspected myocardial ischemia; 1 emphyzema; 1 glaucoma (high eyeball pressure).

ECG tracing showed that: 4 suspected of myocardial ischemia or cardiomyopathy; 5 nonspecific S-T elevation with unknown cause (may be due to previous pericarditis or myocarditis) - need further investigation to confirm our assumption; 1 bradycardia, 1 atrial fibrillation with normal ventricular response.

Biochemical analysis: of all 58 workers who were examined for biological data showed that (Table 1): 1 had hemoglobin content more than 18 gr % and 1 with packed cell volume more than normal (1.7%); red blood cells, kidney function tests and uric acid levels were normal. Ten had SGOT elevation and 11 with SGPT elevation contribute to 17.3% and 19.1% respectively. Lipid profile: 7 had high total cholesterol level with 3 elevated HDL cholesterol less than normal and 8 LDL cholesterol higher than normal, represent respectively 12.1%, 5.1% and 14.1%. Six had triglyceride level higher than 200 mg% (10.4%).

Table 1. Biochemical Data of Workers of a Metal Industry

	Normal Value	Abnormal	Percentage (%)
Hematology:			
Hemoglobin	13.5 - 18.9 gr%	1	1.7 %
Erythrocytes	$(4 - 5.5) \times 10^6/\text{c ml}$	0	0
Packed Cell Volume	40 - 54%	1	1.7 %
Kidney Function:			
Urea-N	< 30 mg %	0	0
Uric Acid	< 7 mg %	0	0
Liver Function:			
SGOT	< 25 IU/l	10	17.3 %
SGPT	< 25 IU/l	11	19.1 %
Lipid Profile:			
Total Cholesterol	< 220 mg %	7	12.1 %
HDL Cholesterol	> 35 mg %	3	5.2 %
LDL Cholesterol	< 150 mg %	8	14.3 %
Triglyceride	< 200 mg %	6	10.4 %

Note: Statistical analysis will be performed following the results of elemental analysis.

Up to present we have blood, nail and hair samples from 58 workers of a metal industry and some airborne particulate samples deposited on Nuclepore filters that are ready for elemental analysis.

PLANS FOR FUTURE WORK

1. Determination of elemental composition of airborne particulate matter, and enrichment factor of the respective elements in airborne particulate samples.
2. Determination of elemental level in dried sera, erythrocyte, hair and nail samples.
3. Preparation of sera, erythrocyte, hair and nail samples from control and determination of elemental levels in these samples.
4. Statistical evaluations to obtain possible correlation among the observed data
5. Further study on the possible health impacts of airborne particulate matter in workplace of an aluminum industry.

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CRP KEN/9478



XA9950305

WORKPLACE MONITORING AND
OCCUPATIONAL HEALTH STUDIES IN KENYA
USING NUCLEAR AND RELATED
ANALYTICAL TECHNIQUES

INSTITUTE OF NUCLEAR SCIENCE
UNIVERSITY OF NAIROBI, KENYA

Chief Scientific Investigator: A.M. KINYUA

OCTOBER 1996 - OCTOBER 1997

HEAVY METAL ANALYSIS OF SUSPENDED PARTICULATE MATTER (SPM) AND OTHER SAMPLES FROM SOME WORKPLACES IN KENYA

Investigators:

A.M. Kinyua, C.K. Gatebe, M.J. Mangala, D.M. Maina, A.K. Korir and S. Bartilol
Institute of Nuclear Science
University of Nairobi,
P.O. Box 30197, Nairobi, Kenya.

R. Kwach, L.N. Njau and E.A. Mukolwe
Kenya Meteorological Department,
P.O. Box 30259, Nairobi, Kenya.

K. Odhiambo
Department of Environmental Science
Kenyatta University
P.O. Box 30 Nairobi, Kenya

V.N. Konji
Department of Biochemistry,
University of Nairobi,
P.O. Box 30197, Nairobi, Kenya.

T. Kwasa
Department of Medicine,
University of Nairobi,
P.O. Box 30197, Nairobi, Kenya.

A. Mware, P.K. Bor and J. K. Wachira
Mines and Geological Department
Ministry of Environment and Natural Resources
P.O. Box 30009
Nairobi, Kenya.

SUMMARY

Air pollution studies in Nairobi are indicating a rising trend in the particulate matter loading. The trend is mainly attributed to increased volume of motor vehicles, the physical change of the environment, agricultural and industrial activities. In this study, total suspended particulate matter sampling at the Nairobi industrial area and inside one workplace are reported. Included also are the results of analysis of water samples and effluents collected from a sugar factory, a tannery, and mercury(Hg) analysis in some beauty creams sold in Nairobi.

The samples were analysed for heavy metal content using Energy Dispersive X-ray Fluorescence (EDXRF) while the suspended particulate matter (SPM) concentrations were determined by gravimetric technique. Total reflection x-ray fluorescence(TRXF), atomic absorption spectrophotometry and PIXE analytical techniques plus the use of Standard and Certified Reference Materials(SRM's and CRM's) were used for quality control, analysis and evaluation of the accrued data.

Air sampling in the industrial area was done twice(Wednesday and Saturday) every week for a period of two months(November and December, 1996) and twice monthly for a period of six months (January-June 1997). Each sample covering approximately 24 hours, was collected using the 'Gent' Stacked Filter Unit (SFU), for day and night times. The SPM were found to vary from 16 to 83 mgm⁻³ during the sampling period.

The analysis of dust collected inside a workplace showed that there was poor filtration of the air pumped into the building and that there was a need for improvement of the air conditioning unit plus reduction of emissions from a neighbouring tyre factory.

Beauty creams analysed showed that there is some mercury present in significant amounts (0.14 - 3.0%). The results of these mercury levels are presented for various brands of cosmetics sold in some market outlets in Nairobi. The health implications on the presence of mercury in some of these beauty creams is also discussed.

The presence of sulphur (0.9 - 439 $\mu\text{g/ml}$) in the water samples from the River Nyando showed that waste from the factories was certainly affecting the water quality of the river. These high levels were registered at a waste treatment pond in the factory. Heavy metal analysis of the water samples collected from River Nyando along the sugar and agro-chemical food industries showed phosphorus and lead (Pb) were below detection limits which ranged from 30-180 $\mu\text{g/ml}$ and 30-150ng/ml respectively. The occurrence of these high levels of sulphur during some sampling visits, suggests some random release of industrial wastes into the river and poor effluent control measures by the industries. Other parameters affected by the industrial wastes included the conductivity, salinity and BOD.

From this study, it is evident that industrial activities and some of their products, motor vehicles and the physical change of the environment are contributing significantly to environmental pollution in Kenya. Particulate matter loading and lead (Pb) levels are found to be higher than those from a previous studies. Whereas it is difficult to pinpoint the exact cause of these increases, the increase in motor vehicle volume, worsening state of our roads, lack of an effective inspection and maintenance programme of motor vehicles and industries in the country, lack of enforcement, supervision and implementation of the Kenya Factory Act provisions, are some of the major causes of this increase. There is therefore a great need for further studies geared towards epidemiological investigations especially among the factory workers, the children and the elderly.

1.0 INTRODUCTION

Cases of occupational asthma, byssinosis, silicosis and asbestosis have been reported in industrial workers (battery manufacturing, cement production, mineral processing) in Nairobi, Athi River, Thika and Mombasa Towns [Kahenya, 1996]. As a result, workers and residents who live near some of these industries have suffered a decline in their standard of living. A number of previous studies have also been done on air pollution [Gatebe and Kinyua, 1994; Muriuki, 1995; Gatebe et al., 1996], water and industrial wastes [Kinyua et al., 1990a; Kinyua and Pacini, 1991; Odhiambo, 1997]. Some recent studies [Kahenya, 1996; Kenny, 1996] have revealed that some occupational diseases are becoming a growing problem in Kenya because of the rapid rate of industrialization coupled with ignorance of the dangers caused by lack of cleaner production practices by some of the local industries.

Pollution of the atmosphere affects the lives of millions of people in all parts of the world, especially those living in large industrialized cities with heavy motor vehicles [Suess and Craxford, 1976; Schwela, 1997]. The World Health Organization lists some of the major environmental problems of urban and industrial areas and their surroundings as: unpleasant fumes and odours, reduced visibility, injury to human health and crops, damage to property by dust and corrosive gases.

In Kenya pollution from motor vehicles especially in the contribution of total suspended particulate matter (TSPM) has become significant only in the urban conditions where there is high traffic density. Lead (Pb), emitted by the motor vehicles, is added in petrol (~ 0.4g/L) as tetraethyl lead to improve combustion characteristics of the petrol air mixture in engines of motor vehicles [Gatebe, 1996]. This increases efficiency of engines with higher compression ratios. Most of this lead is emitted as lead oxide in the exhaust fumes and some of it becomes airborne. The airborne dust can then enter the lungs where it is absorbed into the body.

In Nairobi, like in many other cities in developing countries, there exist gross pollution which is clearly detectable by senses [Lalor et al., 1993]. Motor vehicles have been on the increase over the last few decades and it is suspected that this is accompanied with an increase in levels of motor vehicle pollutants [Gatebe, 1996]. Recent studies have shown rising trends in SPM in the city [Gatebe et al., 1996]. However, the contribution of the SPM arising from motor vehicles has not been effectively quantified. Therefore, it was the aim of this project to sample from the Nairobi industrial area and various workplaces, the suspended particulate matter, analyse it for the heavy metal content and hopefully begin providing assessment data for future epidemiological case studies. The study is also meant to sensitize the authorities and employers in these industries on the dangers posed and also to suggest precautionary measures that can be taken so as to alleviate environmental degradation by way of cleaner production practices.

1.1 Site descriptions

(a) Nairobi Industrial Area

The Nairobi Industrial Area, is shown in the enclosed map (Fig. 1). It is 1798m above mean sea level. The wind directions are mainly easterlies while the atmosphere is neutrally stable. Air sampling at this site is for the period November 1996 - August 1997 and is still going on. This site is located some 13 km from the city center and to the south eastern side of it. It is in the main industrial area of Nairobi. Surrounding it are residential estates of high population densities particularly to the western and north-eastern sides where there are also two main soccer stadiums within ~ 3km. The Jomo Kenyatta International Airport is approximately 5km to the south-western side of this site. It is difficult to give an estimate of the population density around this site, since the information was not available by the time of compiling the data. However, a clever guess can put the density to be around 25000 persons per kilometre.

Within this area are also found various industries (metal, chemical, food processing, etc.). The effluents from 16 industries, two sewage treatment works and various sections of the Nairobi and Athi Rivers have previously sampled and analysed over different periods [Njuguna, 1978; Kinyua et al., 1990a; Kinyua and Pacini, 1991; Kinyua et al., 1997]. Sample collection and preservation was carried out as set by UNEP (1987). Polyethylene containers were used to minimize trace metal contamination.

(b) Voucher Processing Workplace

The Voucher Processing Unit Centre is a modern three storey building for some banking activities. The first two floors have several computer hardware and installations used for processing of the bank's financial transactions. These facilities became operational in March 1997, though they had been installed in January 1997.

The top floor of the building only houses the main air conditioning unit for the Centre. The air conditioner has inlet ducts located on the same side with the diesel power generator exhaust whose outlets face the Prisons Staff Quarters. The Avon Tyre Factory bay and an unpaved road passing next to the premises including other industrial activities are the main neighbours (Figure 2).

On each floor, the rooms in the Centre are separated by partitions of hardboard where computer terminals and peripherals have been installed. These rooms are ventilated, air conditioned and fitted with smoke detectors. The Centre has a back-up power supply from a diesel generator, located on the ground floor. The generator was used continuously in February to May 1997 before an appropriate transformer for the mains supply was installed. For most of the day, the wind direction in Nairobi is north-easterly [Gatebe et al., 1996].

Next to the Centre is the Industrial Area Prisons Department which occasionally burns its rubbish at a site close to the air inlet ducts of an auxiliary air conditioning unit which is ~ 5m high above the ground level. Avon Industries, a tyre manufacturing company is located adjacent to this building separated by a car park. At the time of our visit, the building floors had been cleaned by blowing and sucking by use of a vacuum cleaner. The aim was first to characterize the dust collected by use of heavy and light elemental contents and if possible, pinpoint the dust origin and also to recommend to the client the ways to eliminate this problem so as to protect the workers and the sensitive equipments installed. After rectification of this problem, the next exercise has been to sample the air particulate levels inside and outside this building by way of a portable PM-10 system recently borrowed from Schonland Research Centre for Nuclear Sciences, University of Witwatersrand, Johannesburg, South Africa. This campaign for air particulate monitoring in this building is still going on.

(c) Sugar, Food and Chemical Factory

This site is at Muhoroni which is about 400 km from Nairobi in western Kenya. It is located near Lake Victoria in the sugar belt of Kenya along the River Nyando where a lot of sugar and other agro-chemical based industries have been built. Four sampling points were selected (Fig. 3).

2. SAMPLING

(a) Total Suspended Particulate Matter (TSPM)

Sampling of SPM was done using a 'Gent' Stacked Filter Unit [Maenhaut, 1993] and as previously described [Gatebe et al., 1996]. Nucleopore filter membranes (0.4mm, and 8mm) were weighed in an air conditioned laboratory controlled at 50% relative humidity and 20°C. A ²⁴¹Am α -emitting source (5mCi)

was used to remove the static build up from the filter. Prior to weighing, all filters were left to equilibrate for at least 24 hours. Before the start of each sampling exercise, the SFU was properly cleaned with ethanol to remove any particles which may have previously embedded inside. Filters were handled with care using plastic tweezers to avoid grease from fingers and heavy metal contamination. Information recorded was: (i) volume of air sucked by the pump and (ii) average weather conditions. During the sampling, the sampler was run at flow rate of 1m³/hour for 24h sample collection (24m³).

(b) Voucher Processing Workplace

A total of 14 samples were sampled all together. Four(4) were collected on 7th August, 1997 and nine(9) samples on 15th August, 1997. Eleven(11) of these were cotton swaps that had been wiped on surfaces which had accumulated dust. The swaps were from the computer peripherals, the furniture, air inlet ducts, car park pavement and at the main air conditioner radiator. The Server Unit had also previously been sampled by the Client and a sample submitted to the Institute of Nuclear Science for analysis. This sample was reportedly obtained before the rooms had been cleaned since January 1997.

Sample	Description/Colour
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A	Sampled on cotton swap from the top of the monitor in the computer server room by the client on 18th July 1997 (black).
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B	Collected on cotton swap from the top of a cabinet in the computer server room on ground floor (black).
---	---

C	Collected on cotton swap from the top of a cabinet in the computer server room on ground floor (black).
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D	Collected on cotton swap from the top of the door entrance to the computer server room on ground floor (black).
---	---

E	Collected on cotton swap from an air conditioning room on top floor of the building (brown).
---	--

F	Collected on cotton swap from the top of the router cabinet in the server room (black dust).
---	--

G	Mixture of soil and a tyre factory wastes sample collected on "murram road" behind Avon Factory (black).
---	--

H	Cotton swap dust sample from the back-up power supply generator room (brown).
---	---

I	Charred factory waste sample (black) from a smouldering "rubbish pit" next to the murram road near the loading bay of the tyre factory.
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J	Cotton swap sample from the air inlet duct in the back-up power supply generator room (brown).
---	--

L	Soil sample from the "murram road" passing next to the Centre. Avon Factory (brown).
---	--

M	Cotton swap sample from the air conditioner room (brown dust).
---	--

N	Cotton swap sample from the radiator of the air conditioner room (brown dust).
---	--

O	Cotton swap sample from the car park pavement between Avon Industry and Centre (black).
---	---

(c) Sugar, Food and Chemical Factory

Four sampling points were selected. Sampling was done for two weeks and 15 samples collected and analyzed for BOD, DO, TDS, hardness, salinity, conductivity, pH, and heavy metals by TXRF technique. After a visit to the factories and survey of the points of discharge and waste treatment ponds, sampling points were established as shown in Fig. 3:

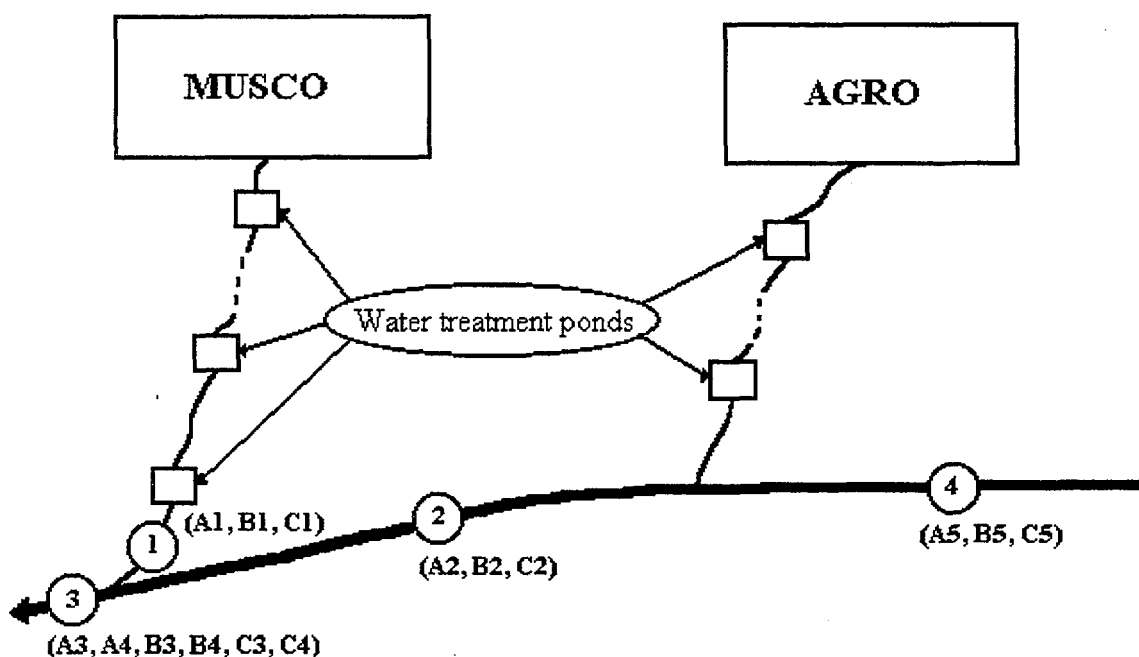


Figure 3. Sampling points in the study

Point 1 at the outlet of the last (ninth) waste treatment to determine its efficiency. Samples A1, B1 and C1 were taken at this point;

Point 2 at a distance from the Agro-Chemicals and Food Factory on the downstream but before that of Muhoroni Sugar Factory. This point was established to take care of the waste discharged by the Agro-Chemicals and food factory. Samples A2, B2 and C2 were taken from this point;

point 3 at the discharge point of Muhoroni Sugar Factory. Samples A3, A4, B3, B4, C3 and C4 were taken from this point;

Point 4 at about 1/2 km away from the discharge point of the Agro-Chemicals Factory upstream. Samples A5, B5 and C5 were taken from this point.

Water samples were collected using one litre polyethylene plastic bottles, which had been thoroughly washed with water and 10 % nitric acid then rinsed with copious amounts of double distilled water [Maina et al., 1997]. In the field, the water bottles were washed with the water being sampled before actual samples were taken. The water bottles were immersed closed then opened at a depth of about 20 cm from the surface to avoid contamination by surface debris [Maina et al., 1997].

(d) Beauty Cream Samples

Samples (n=100) of beauty creams were bought randomly from various retail shops in Nairobi and its environs [Kinyua et al., 1996]. Each sample was under its normal package/protection cover and suffered no atmospheric exposure that would lead to contamination and deterioration. Each sample was squeezed into a clean beaker then heated on a water bath at 40-50°C until melting was complete. The melt was then poured onto a 2.5 cm diameter Mylar (Spectro - Film grade: Somar INC., USA) supported on aluminium ring [Kinyua et al., 1994] so as to acquire the configuration of a homogenous pellet (0.3g/cm²) when cooled. No other physical and/or chemical treatments were applied to the sample.

The EDXRF system utilized in this analyses has previously been described [Kinyua, 1982]. It consists of 28 mm² x 5 mm thick Ortec Si(Li) detector with beryllium window thickness of 25 µm, a Canberra amplifier/pulse processor with pile-up rejector Model 2020, and a Canberra S100 PC based multichannel analyzer system. The detector resolution (full width at half maximum-FWHM) was 190 eV at Mn K_a line at 5.9 keV, while the pulse shape time constant was 10 µs. The excitation source was ¹⁰⁹Cd (20mCi) with a run time of 300 seconds.

The spectra data deconvolution was by AXIL based software [IAEA, 1995], while quantitative analysis was by QAES Software [Kump, 1993]. The detector system was calibrated using an oil standard

reference material - NIST-SRM-1634b and some in-house standards for L-lines. Calculation of the mercury concentration in the samples was based on intensity recorded (I), being taken as equal to a product of sensitivity (S), concentration of a given element (C), absorption coefficient (A), and enhancement factor (E) [Kump, 1993]. For mercury, enhancement is absent ($E=1$) since there is no additional excitation of mercury by other fluorescent radiation emitted by other elements present in the sample. The absorption correction factor was measured experimentally by use of pure target of molybdenum, whereas the sensitivity curve was generated from the use of the oil standard reference material and in-house standard for other L-lines which were not present in the oil standard. The intensity (area under the mercury peak) was read from the spectrum fitting by AXIL.

(e) *Nairobi Industrial Effluents*

A recent study [Kinyua et al., 1997] analysing water samples collected on the up-and-down streams of a tannery factory discharge point into Kamiti river has been done. The heavy metal analysis was done by TXRF as previously explained [Korir, 1997] while BOD and COD parameters were done as per the standard method for the examination of water and waste water [Rad et al., 1975]. Sample collection, storage and preservation was carried out as set out previously [UNEP, 1987]. Polyethylene containers were used minimize trace metal contamination. Sample preparation for analysis was carried out within 48 hours.

3. SAMPLES ANALYSIS

3.1 *Main Analytical Techniques used*

a) *Energy Dispersive X-Ray Fluorescence (EDXRF)*

The EDXRF system has previously been described [Kinyua, 1982]. The samples were irradiated for 3000 seconds and the spectra data were stored in a computer. Spectra de-convolution and fitting was carried out by AXIL (Analysis of X-ray Spectra by Iterative Least-Squares Fitting) modular program of the Quantitative X-ray Analysis System (QXAS) [IAEA, 1995], while quantitative analysis was by a software for Quantitative Analysis of Environmental Samples (QAES) [Kump, 1993]. Quality control assessment of the technique was done by analysis of standard reference material from National Institute of Standards and Technology (NIST), SRM 2676d.

b) *Total Reflection X-ray Fluorescence*

Sample preparation

The system used for this work is as described previously [Korir, 1997]. One ml of each sample was pipetted onto a clean vial and 1 μg of cobalt per ml of sample was added as internal standard. The content of the vial was mixed thoroughly by shaking and after which 10 μl was pipetted on a cleaned sample carrier. The samples were seen to spread to about 6 mm in diameter. The sample substrate liquid was then dried in a soft vacuum at room temperature (23 °C). For each sample, 3-4 replicates were measured.

Preconcentration of water samples

The pH of 100ml of the sample, with 10 μg of Co internal standard and 5 μg of Ni added as a carrier, was adjusted to between 5 and 6. 10 ml of freshly prepared 2% NaDDTC solution was added and stirred for 15 minutes. The precipitate formed was filtered on millipore filter of porosity 0.4 μm . The filter substrate formed was dissolved in 1 ml of MIBK solution into a clean container. 10 μl of the solution was spiked onto each of the clean sample carriers, dried and analysed.

Instrumentation

The analysis was carried out using the Vienna Prototype TXRF Module attached to the line focus of the Type D Housing of Mo target water cooled Siemens Model FK 60-04 X-ray tube. The high voltage generator used was the Kristalloflex 710H from Siemens with maximum 53.5 kV and current 40 mA. The x-ray detector used was Canberra Si(Li) Model 2008 of resolution 174 eV (Mn- K_{α} line), active crystal volume of 30 mm² and thickness 5mm. For this study, the x-ray tube used was operated at 40 kV and 20 mA. No other extra spectral modification of the Mo primary beam was done due to the low beam intensity. The TXRF module was optimised for the Mo-K lines with the cut off achieved at 20.0 keV. The angle of incident with the sample used was about 0.6 mrad. The counting dead time for most samples

averaged 1%. X-ray spectra were collected for 2000s in MCA emulation software - S100 from the Canberra. The quantitative analysis was done with the analysis package, QXAS[IAEA, 1995] after calibration of the spectrometer using a set of multi-element standard solutions with Co as internal standard [Kregsamer, 1995]. The sample carriers used were the suprasil discs, 30 mm in diameter and 3 mm thick.

c) Gravimetric

The fine and coarse fraction mass concentrations were obtained through gravimetric measurements of the nucleopore filter membranes with 1 mg sensitivity (Ainsworth, Type 24N) weighing balance. Before weighing, the filters were equilibrated for 24 hours at 50% relative humidity and 20°C temperature. Electrostatic charges were controlled by use of ²⁴¹Am radioactive source(5μCi). The filter membranes were then weighed before and after air filtration.

d) Carbon and Sulphur Analysis

Carbon and sulphur contents in the cotton swap samples were analysed using a Carbon-Sulphur analysis system (CS-244- LECO Corporation, USA). The system used consists of :

- (i) an induction furnace -to oxidise the carbon and sulphur in the samples to CO₂ and SO₂ at high temp (500°C);
- (ii) measurement unit : for CO₂ and SO₂ detection and determination of sample weight;
- (iii) control console: a microprocessor based instrument pre-programmed for measurements of C and S after calibration with standards. The accuracy and sensitivity of the system is ±5% for levels <0.1%C and ±2% for levels >0.1% C.

3.2 Techniques used for Quality Control and Intercomparison with EDXRF Results

a) Total Reflection X-ray Fluorescence (TXRF)

The TXRF system used is as described above. Standard reference materials, water and other digested samples were prepared for analysis as previously discussed [Korir, 1997].

b) Atomic Absorption Spectrophotometry (AAS)

The AAS unit used in this work as previously been described [Jumba, 1980]. It is a Perkin Elmer Model 2380 a microprocessor controlled AAS, which measures the concentration of metallic elements and provides integrated readings in absorbency and concentration. For this work, intercomparison and verification of results of the mercury levels in beauty creams, a few of the samples were extracted and analysed using an alternative technique as previously described [Wandiga and Jumba, 1982]. Aliquots (0.5g) were digested first with H₂SO₄ (1 hr) and then 6% aqueous potassium permanganate(2 hrs). The excess permanganate was destroyed with hydroxylamine and the aqueous extract analysed by flameless cold vapour atomic absorption spectrometry (AAS) - Pye Unicam SP 90A, at 253.7nm. The detection limit obtained was better than 4 ng.

c) Particle Induced X-ray Emission (PIXE)

Ten samples were analysed using a tandem accelerator facility at Schonland Research Centre for Nuclear Science, University of Witwatersrand, South Africa. The samples which had earlier been analysed with EDXRF, were cut into an area of 2.7cm² using a punch. A Proton beam (collimated with a rectangular collimator) with an energy of 3.2 MeV, and a beam current of 10nA was used. Irradiation times were 600 seconds. The PIXE system was calibrated by a large number of Micromatter Standards (mono and bielemental) of known area density (5% uncertainties certified). The fitting of the x-ray spectra and quantitative analysis were performed using the AXIL-PC software and WITS-HEX [Lipworth et al., 1993].

4. RESULTS AND DISCUSSION

4.1 Quality Control Measurements

4.1.1 EDXRF and PIXE Analysis of TSPM and SRM Materials

For both PIXE and EDXRF analytical systems, the detection limits were based on three sigma criterion [Wobrauschek, 1995]. Detection limits for PIXE are typically 5 ng/m^3 for elements in the range $13 < Z < 22$ and 0.4 ng/m^3 for elements with $Z > 23$. These detection limits were calculated based on a sampling flow rate of 20 litres per minute, 12 hours of sampling and irradiation time of 600 seconds. Table I shows the analytical results of SRM-2676d and the detection limit for the EDXRF based on the above criterion. Figure 4 shows the plot of EDXRF results versus the SRM values. The correlation coefficient between these two values was about 98%. Figure 5 and Table II shows an intercomparison of the analytical results of the analysis of coarse and fine filters by both PIXE and EDXRF techniques. There was some good agreement in some of the results especially the major elements such as iron. The differences noticed in some of the results are mainly due to falling of the sample material during transportation, preparation and inhomogeneity. However, the precision of the elemental concentration measurements is typically less than 10% for elements with concentration near the detection limit.

Table 1(a) EDXRF analysis of a Standard Reference Material - NIST 2676d: metals on filter media

Element	Expt. Value ($\mu\text{g}/\text{filter}$)	Certified Value($\mu\text{g}/\text{filter}$)	Filter Number
Mn	16.06 ± 0.41	19.83 ± 0.38	III
Zn	82.05 ± 1.52	99.31 ± 1.77	III
Pb	26.55 ± 0.72	29.77 ± 0.61	III
Mn	10.54 ± 0.21	9.83 ± 0.14	II
Zn	55.54 ± 0.83	49.47 ± 0.73	II
Pb	17.76 ± 0.34	14.82 ± 0.26	II
Mn	2.84 ± 0.05	2.09 ± 0.03	I
Zn	13.33 ± 0.18	10.17 ± 0.13	I
Pb	10.84 ± 0.15	7.44 ± 0.10	I

Table 1(b) Experimental Detection Limits for EDXRF

Element	Atomic Number	Detection Limits($\mu\text{g}/\text{filter}$)	Detection Limits(ng/m^3)*
Ca	20	2.15 ± 0.21	89.5 ± 8.5
Mn	25	0.41 ± 0.03	17.0 ± 1.0
Fe	26	0.33 ± 0.01	13.5 ± 0.5
Cu	29	0.18 ± 0.03	7.5 ± 1.5
Zn	30	0.15 ± 0.02	6.0 ± 1.0
Pb	82	0.19 ± 0.02	8.0 ± 1.0

Nb: * - based on 24h sample collection (24 m^3) if flow rate is $1\text{ m}^3/\text{hour}$ using Gent SFU

Table 2: Comparison of EDXRF and PIXE Analysis of Aerosols Samples($\mu\text{g}/\text{m}^3$)

Element	Fine Filter ($0.4\mu\text{m}$)		Coarse Filter ($8\mu\text{m}$)		Period
	EDXRF	PIXE	EDXRF	PIXE	
K	0.0956	0.167	0.544	0.667	Night 1
Mn	0.0629	0.014	0.0765	0.108	"
Fe	0.165	0.149	0.909	1.154	"
Zn	0.177	0.137	0.119	0.153	"
Pb	0.0741	0.047	0.0944	DL	"
K	0.187	0.075	0.517	0.317	Day 2
Mn	0.0752	DL	0.0752	0.021	"
Fe	0.137	0.061	0.322	0.247	"
Zn	0.0852	0.036	0.028	0.026	"
K	0.60	0.159	0.0305	0.229	Day 4
Mn	0.107	0.015	0.187	0.047	"
Fe	0.151	0.145	0.549	0.54	"
Zn	0.133	0.147	0.109	0.045	"
K	0.20	0.106	0.0751	0.319	Night 4
Mn	0.0678	DL	0.0619	0.064	"
Fe	0.0992	0.048	0.64	0.693	"
Zn	0.0637	0.024	0.0679	0.055	"
K	0.0221	0.068	0.409	0.072	Day 5
Mn	0.0661	DL	0.12	DL	"
Fe	0.0671	0.05	0.231	2.219	"

Nb: DL - Detection limit

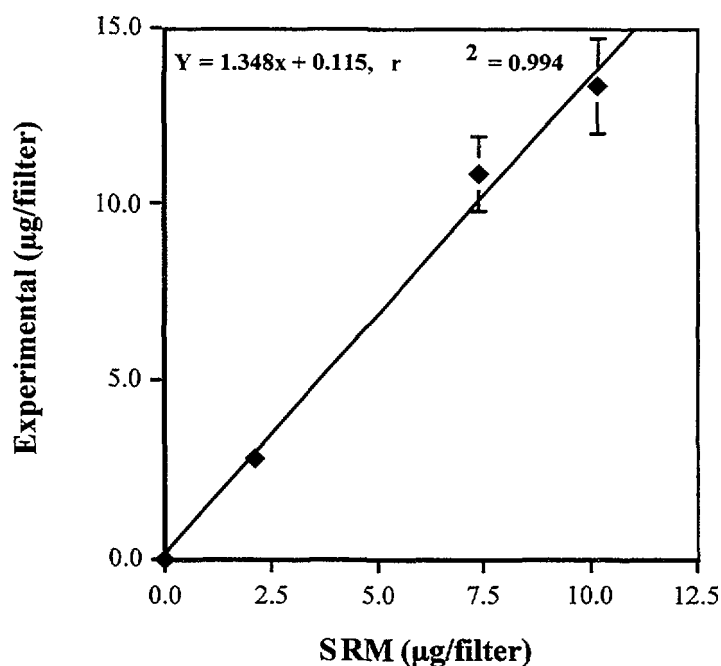


Figure 4 Comparison of EDXRF Results(Mn,Pb) with those of NIST 2676d Standard

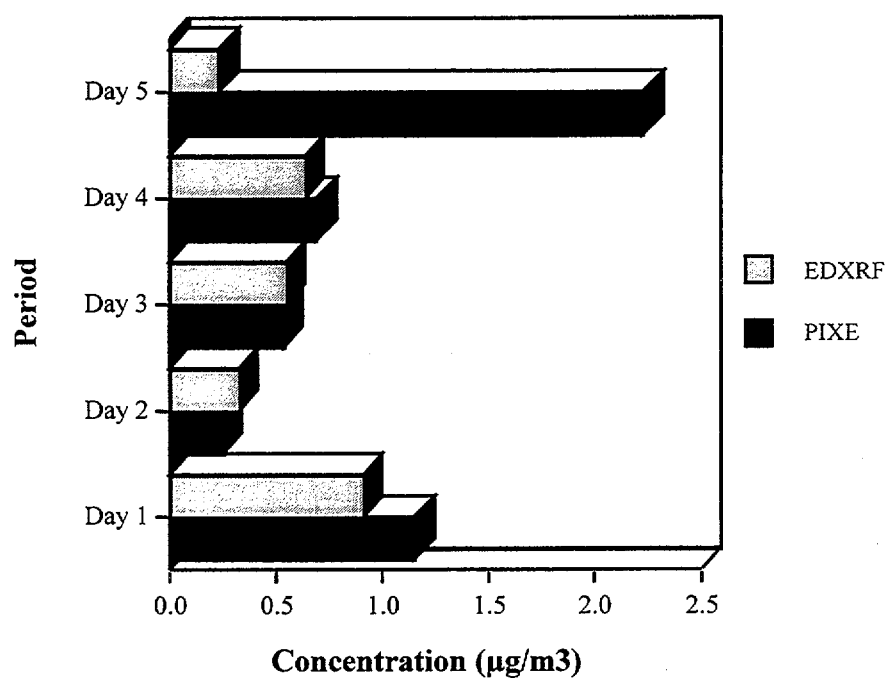


Figure 5 Comparison of EDXRF and PIXE Results for Iron in Coarse Filter

4.1.2 EDXRF and AAS of Cosmetic Creams

The correlation between the mercury analytical results obtained by intercomparison of EDXRF and cold vapour AAS techniques was better than 95 % for the samples analysed (Fig. 6).

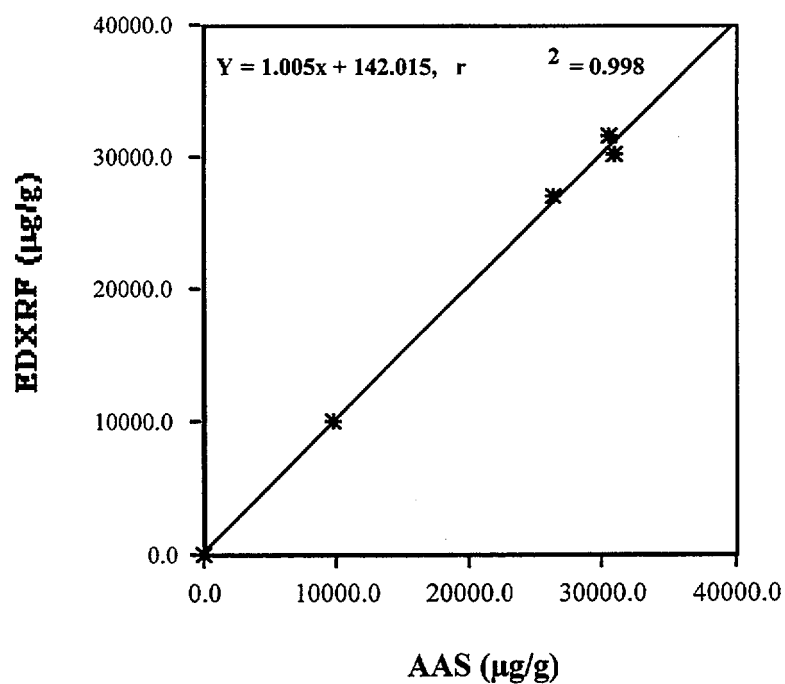


Figure 6 Comparison of EDXRF and AAS Results of Mercury analysis

4.1.3 TXRF of Standard Reference Materials and Laboratory Water Standards

4.1.3.1 TXRF analysis of Standard Reference Materials

The analysis of various standards including those from in-house preparations, are as shown below:

Table 3. Values for Lyophilised Pig Kidney (BCR No.186)

Element	Experimental($\mu\text{g/g}$)	Certified($\mu\text{g/g}$)	LLD*
Mn	7.4 ± 0.4	8.5 ± 0.3	0.7
Fe	275 ± 11	299 ± 10	0.8
Cu	31.6 ± 0.5	31.9 ± 0.4	1.4
Zn	134 ± 6	128 ± 3	1.4
Se	9.7 ± 0.5	10.3 ± 0.5	1.4

Table 4. Values of concentration for Chinese Human Hair (GBW 09101)

Element	Experimental($\mu\text{g/g}$)	Certified($\mu\text{g/g}$)	LLD*
Ca	1022 ± 69	1090 ± 721	2.7
Cr	3.2 ± 0.3	4.8 ± 0.4	0.9
Mn	3.6 ± 1.0	2.9 ± 0.2	0.7
Fe	71.0 ± 5	71.2 ± 6.6	0.8
Ni	3.4 ± 0.2	3.2 ± 0.4	1.3
Cu	23.0 ± 0.8	23.0 ± 1.4	1.4
Zn	194 ± 5	189 ± 8	1.5
Sr	5.7 ± 0.5	4.2 ± 0.1	2.4
Pb	11 ± 1	7.2 ± 0.7	5.2

Table 5. Concentration values in $\mu\text{g/g}$ for Rye Flour (IAEA/ V-8)

Element	Experimental value	Certified value	LLD*
K	2320 ± 191	1925 ± 135	1.3
Ca	142 ± 4	149 ± 10	0.5
Mn	2.1 ± 0.1	2.06 ± 0.12	0.1
Fe	5.3 ± 0.5	4.1 ± 0.7	0.1
Cu	0.75 ± 0.03	0.95 ± 0.19	0.3
Zn	2.65 ± 0.2	2.53 ± 0.33	0.2
Br	0.31 ± 0.1	0.38 ± 0.07	0.2
Rb	0.55 ± 0.04	0.48 ± 0.07	0.2

Table 6. Values for 'rice-unpolished' (NIES No. 10(a))

Element	Experimental($\mu\text{g/g}$)	Certified($\mu\text{g/g}$)	LLD*
K	1875 ± 73	1800 ± 80	5
Ca	100 ± 4	93 ± 3	3
Mn	31.3 ± 0.7	34.7 ± 2	0.5
Cu	7.9 ± 0.2	3.5 ± 0.3	0.6
Zn	24.8 ± 0.5	25.2 ± 0.8	0.6
Rb	4.4 ± 0.4	4.5 ± 0.3	0.6

Table 7. Values of concentration for Japanese Tea(NIES No.7)

Element	Experimental($\mu\text{g/g}$)	Certified($\mu\text{g/g}$)	LLD*
K	18850 ± 784	18600 ± 700	10
Ca	3131 ± 22	3200 ± 120	7
Mn	627 ± 10	700 ± 25	1.4
Ni	4.6 ± 0.3	6.5 ± 0.3	1.4
Cu	6.3 ± 0.3	7.0 ± 0.3	1.4
Zn	35.8 ± 1	33.0 ± 3	1.4

Table 8 Concentration values for Kale (IAEA/S636F)

Element	Experimental($\mu\text{g/g}$)	Certified($\mu\text{g/g}$)	LLD*
K	25909 ± 2922	24370 ± 1452	13
Ca	38914 ± 4383	41060 ± 2220	9
Mn	15.4 ± 0.8	14.8 ± 1.68	2
Fe	81.5 ± 8	119.3 ± 14.8	2
Cu	3.4 ± 0.9	4.9 ± 0.63	2
Zn	32.0 ± 2	32.3 ± 2.8	2
Br	15.0 ± 2	24.9 ± 2.5	2
Rb	57.3 ± 5	53.4 ± 5.5	2
Sr	76.4 ± 6	75.7 ± 29.3	1

* limit of detection

Table 9 TXRF analysis of a In-house Water Standard

Element	Experimental(μg)	Expected value(μg)
Ti	3.18 ± 0.04	4.0
Fe	4.25 ± 0.03	"
Ni	4.17 ± 0.03	"
Cu	3.65 ± 0.03	"
Zn	3.86 ± 0.03	"
Sr	3.43 ± 0.03	"
Pb	3.46 ± 0.05	"

Table 10 EDXRF analysis of an In-house Water Standard

Element	Experimental (ppb)	Expected value(ppb)
Ti	84.1 ± 21.5	100
Fe	125.0 ± 11.3	"
Cu	105.0 ± 8.6	"
Zn	78.7 ± 6.6	"
Pb	108.0 ± 8.2	"

4.2 Air Particulate Monitoring

4.2.1 Nairobi Industrial Area Site

4.2.1.1 TSP and Heavy Metal Analysis

Results over the eight months of sampling shows almost similar trends for all the elements Figs. 7-14. (Please see at end of country report) The concentration of Potassium(K), Calcium(Ca), and Iron(Fe) varies from 0.2 to 2 $\mu\text{g}/\text{m}^3$, with Ca showing a higher level than Fe and K over the entire period.

Zinc(Zn) is conspicuously high in all the months varying from 1.0 to 8 $\mu\text{g}/\text{m}^3$. This points out to presence of an industry(ies) dealing or producing Zn or its products. Comparison of these results with the ones from the suburban site(see previous CRP reports and Gatebe et al, 1996) shows higher concentration levels for most elements. This indicates some enrichment from the industries around the sampling site in the industrial area. With this data it will now be possible to sensitize the government on the need to monitor closely the impact of the industries on our air quality.

4.2.2 Voucher Processing Workplace

4.2.2.1 Sample characteristics and other general observations

- (i) Dust samples from the Computer Server room were "black" in appearance.
- (ii) Dust samples from the air conditioner located on top floor and from the back-up power supply room were brown in colour.
- (iii) The dusty "black" samples are fine powder that can easily be transported in air. However, due to the small quantities collected, these samples were not determined for their particle sizes.

4.2.2.2 Heavy Metal Analysis

A total of 10 elements in the samples after analysis with x-ray fluorescence method(EDXRF) are reported. These elements are: potassium(K), calcium(Ca), titanium(Ti), manganese(Mn), iron (Fe), copper(Cu), zinc(Zn), bromine(Br), lead(Pb). Tables 11 and 12 are results of these analysis.

Table 11: Relative elemental intensities(c/s/g)

Ele	A	B	C	D	E	F	H	J	M	N	O	BL
K	-	0.45	0.23	-	0.05	0.11	0.65	0.57	0.21	0.10	0.39	0.02
Ca	1.64	2.11	1.83	0.56	0.55	0.79	1.79	1.72	0.66	0.48	1.44	0.23
Ti	0.25	0.29	0.36	0.07	0.13	0.17	0.87	0.69	0.26	0.18	0.48	0.03
Mn	0.33	0.49	0.47	0.07	0.31	0.16	2.04	1.54	0.71	0.48	1.07	0.05
Fe	4.87	9.07	10.53	2.23	7.49	4.61	43.17	31.12	13.65	10.69	23.33	0.82
Cu	0.14	0.32	0.15	0.10	0.49	0.11	0.30	0.21	0.09	0.12	0.15	0.08
Zn	1.43	2.27	2.60	0.42	2.61	1.35	2.01	1.56	2.13	0.85	2.01	0.16
Br	0.33	0.32	0.28	-	0.08	0.29	0.25	0.19	0.08	0.16	0.02	0.04
Rb	-	-	-	-	-	-	0.67	0.37	0.14	0.12	0.28	0.02
Sr	0.92	0.83	0.61	0.56	0.35	0.40	1.40	0.86	0.42	0.39	0.80	0.28
Y	-	-	-	-	-	0.10	0.44	0.30	0.10	0.10	0.24	0.03
Zr	0.66	0.78	0.92	0.13	0.93	0.44	6.77	3.85	1.76	1.36	3.15	0.06
Pb	0.43	0.36	0.47	0.15	0.14	0.27	1.00	0.60	0.26	0.33	0.44	0.06

- (i) Samples A, B, C, D, F (all from the Server room) have similar matrix and are from the same source.
- (ii) Samples E, H, J, M and N (from the air conditioner and generator rooms) have high levels of crustacean elements:- potassium (K), calcium(Ca), iron(Fe) as compared to the other samples. This suggests air dust as the possible source.

4.2.2.3 Carbon and Sulphur

- (i) Samples G and I (Table 12) contain high levels of carbon and sulphur. The values are : carbon 79% and 2.54% sulphur for sample G and 4.97% carbon and 0.13% sulphur for sample I.
- (ii) The ratio of carbon to sulphur in the samples G and I are: 38.2 and 31.1 respectively which implies that carbon and sulphur in these samples have same origin.

Table 12: Elemental concentration values in mg/g (else in %)

Element	Sample G	Sample I	Sample L
C	4.97%	79%	-
S	0.13%	2.54%	-
K	(3.4 ± 0.3)%	(0.6 ± 0.1)%	5.11 ± 0.5)%
Ca	(3.14 ± 0.3)%	(0.57 ± 0.03)%	(2.8 ± 0.4)%
Ti	(0.4 ± 0.1)%	-	(0.49 ± 0.06)%
Mn	(0.17 ± 0.02)%	(0.36 ± 0.01)%	(0.47 ± 0.01)%
Fe	(2.7 ± 0.1)%	(0.16 ± 0.01)%	(4.28 ± 0.06)%
Cu	27.0 ± 1.0	< 10	37 ± 4
Zn	638 ± 27	(4.9 ± 0.2)%	218 ± 29
Br	-	118 ± 13	5.6 ± 0.3
Rb	50 ± 4	7.8 ± 0.3	69 ± 2
Sr	216 ± 8	13.5 ± 3	173 ± 2
Y	27.0 ± 1.0	-	37 ± 2
Zr	353 ± 23	11.2 ± 1	527 ± 2
Pb	62 ± 6	89 ± 7	68 ± 3

4.2.2.4 Discussion

- Samples from the air conditioner room (E, M and N) and the back-up power generator room (H and J) are of similar matrix but heavily loaded with particulate matter as suggested by enrichment in the samples with iron(Fe), calcium(Ca), manganese(Mn) and potassium(K). Construction activities and unpaved roads in the area all contribute to increased dust particles in the air. Other air polluting activities include; industrial and traffic emissions [Gatebe et al., 1996].
- There was no significant differences in results of heavy metal analysis of the samples collected by the Consultant and that by the Client. This in principle is an indication that the samples are of similar matrix and composition.
- There is no significant reductions in the levels of heavy metals; iron (Fe), zirconium(Zr) and zinc(Zn) for samples collected from the Air Conditioner room and those from the Server room. This implies poor filtration of the air.
- Carbon and sulphur in the samples seem to be of the same origin.

4.2.2.5 Recommendations

- The air filtration system in the premises is not efficient due to the following:
 - the room entrances and exits were not properly constructed so as not to allow the dust inside.
 - openings on the ground floor for cable installations were not properly sealed against the dust.

We therefore recommended a closed /or open-loop air filtration system for the premises. This system is capable of filtering out air particles sizes less than 10µm or less depending on the filter material installed (Fig.15 and 16).
- It was recommended that the floors in the premises be carpeted.
- It was recommended that some dialogue and negotiations on the possible ways and means to reduce the particulate matter in air by way of clean production practices be initiated between the bank, the neighbouring firms and relevant authorities.

4.3 Sugar, Food and Chemical Factory

4.3.1 Heavy Metal Analysis

Results of heavy metal analysis of the water samples collected from River Nyando along the sugar and agro-chemical food industries are shown in Table 13. Phosphorus and lead(Pb) were below detection limits which ranged from 30-180 µg/ml and 30-150ng/ml respectively. The presence of sulphur in these water samples was an indicator of poor effluent control measures by the industries.

Table 13. Elemental Analytical Results in $\mu\text{g/ml}$ (ppm)

Sample	Phosphorous	Sulphur	Calcium	Lead
A1	DL	3.6 ± 0.5	99 ± 2	DL
A2	"	0.90 ± 0.02	16 ± 0.6	"
A3	"	1.2 ± 0.2	18 ± 0.1	"
A4	"	1.1 ± 0.2	18 ± 0.5	"
A5	"	1.1 ± 0.3	18 ± 0.02	"
B1	"	439 ± 2	47 ± 1.0	1.46 ± 0.1
B2	"	182 ± 2.3	19 ± 1.0	DL
B3	"	190 ± 4.2	18 ± 1.3	"
B4	"	259 ± 4.7	20 ± 3	"
B5	"	166 ± 14	17 ± 0.1	"
C1	"	169 ± 5	88 ± 3.8	"
C2	"	164 ± 20	13 ± 1.1	"
C3	"	434 ± 2.2	36 ± 2.3	"
C4	"	228 ± 8.1	31 ± 1.6	"
C5	"	165 ± 13.1	13.9 ± 0.3	"

DL* - detection limit

4.3.2 Other Measurements

Table 14 shows measurements of conductivity, pH, salinity, total dissolved solids(TDS), hardness, biochemical oxygen demand(BOD) and dissolved oxygen(DO). The pH remained relatively very basic in most of the samples analysed. However, the conductivity levels of industrial effluents(A1,B1,C1) were about four(4) times those of the river water while the salinity levels were about eight(8) times. The BOD levels of the waste from the sugar factory is about 100 times that of the river water before any industrial waste discharge while that from the agro industry is about 13 times that of the river water (A5,B5,C5). Although the river seems to recover, the industrial wastes certainly do elevate the BOD levels of the river waters. The requires constant monitoring to ensure that the limits are not exceeded.

Table 14 Results of other Parameters

Sample	Conductivity (mg/l)	pH	Salinity (mg/l)	TDS (mg/l)	Hardness (mg/l)	B.O.D. (mg/l)	D.O. (mg/l)
A5*	246	7.31	0.1	116	124	15	4.4
B5*	140	8.02	0.1	102	126	50	2.0
C5*	237	7.26	0.1	109	118	10	4.2
A2**	205	8.65	0.1	97	84	380	2.8
B2**	321	8.3	0.1	187	99	420	3.6
C2**	188	8.07	0.1	82	91	320	2.6
A1#	1344	7.30	0.7	654	184	2640	1.6
B1#	1286	9.6	0.9	715	193	2450	1.8
C1#	1256	6.9	0.9	701	203	2360	1.8
A3##	201	9.01	0.1	103	92	250	2.4
A4##	233	8.03	0.1	110	98	30	2.2
B3##	302	8.1	0.1	115	89	310	2.0
B4##	285	7.9	0.1	132	72	305	2.0
C3##	192	9.2	0.1	121	81	300	2.2
C4##	201	8.11	0.1	97	104	25	2.4

Key: * - Samples collected before factory discharge points
 ** - Samples collected after the Agro-chemical discharge point
 # - Samples collected after waste treatment ponds of the sugar factory
 ## - Samples collected after the discharge point of the sugar factory

4.4 Beauty Creams

4.4.1 Mercury Analysis

The results of mercury analysis are shown in Fig.17. Typical spectra of cosmetic products analyzed is shown in Fig. 18. Elemental sensitivity for the EDXRF system used is shown in Fig. 19 while the absorption correction factors for mercury varied between 1.5 and 1.8 implying light matrix samples. The enhancement correction factor was taken to be 1 because no other heavy metal was present in most of the samples to additionally excite mercury L-lines.

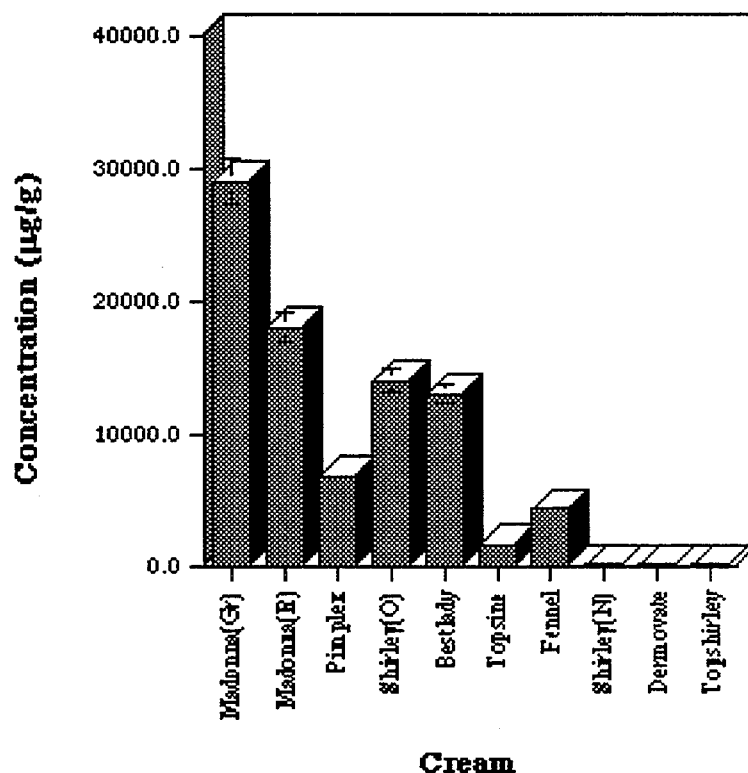


Fig. 17. Mercury levels in Beauty Creams

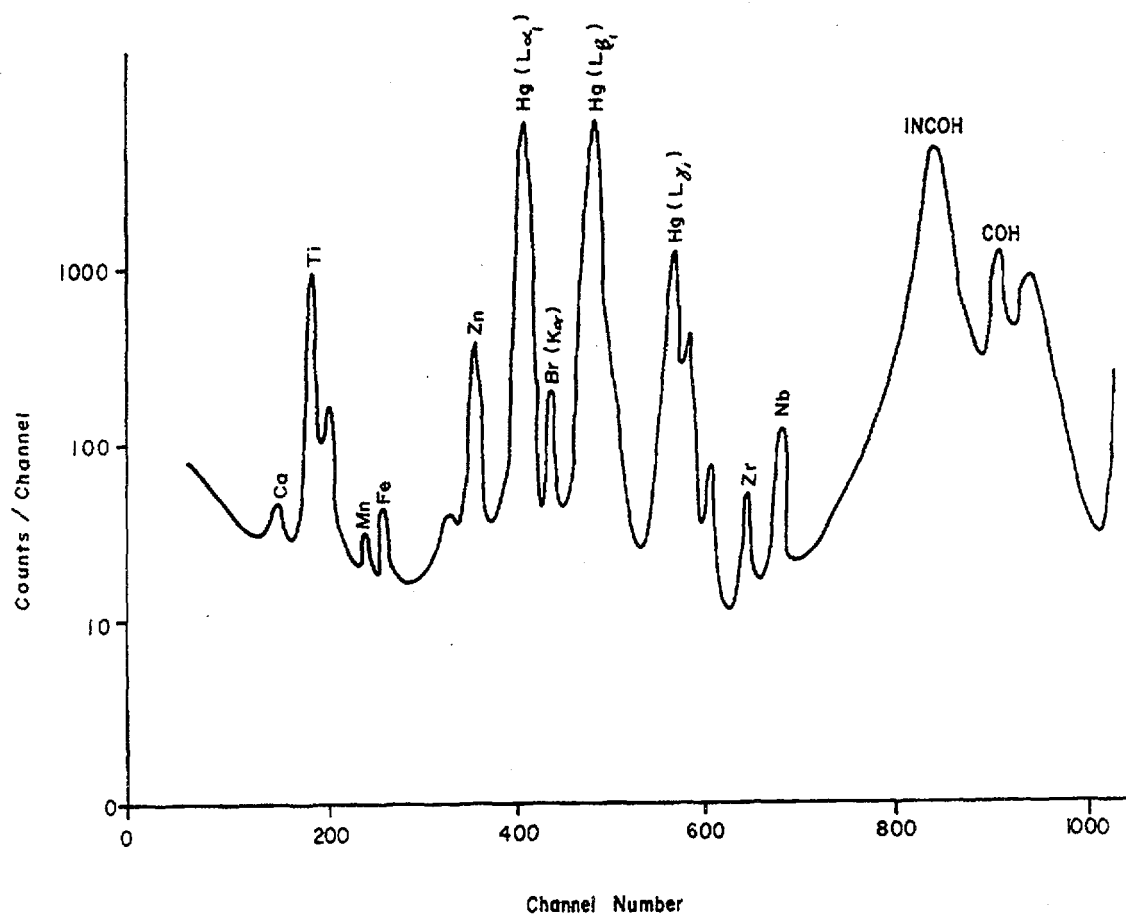


Fig. 18 Typical EDXRF Spectrum of "Madonna"(Green) Sample

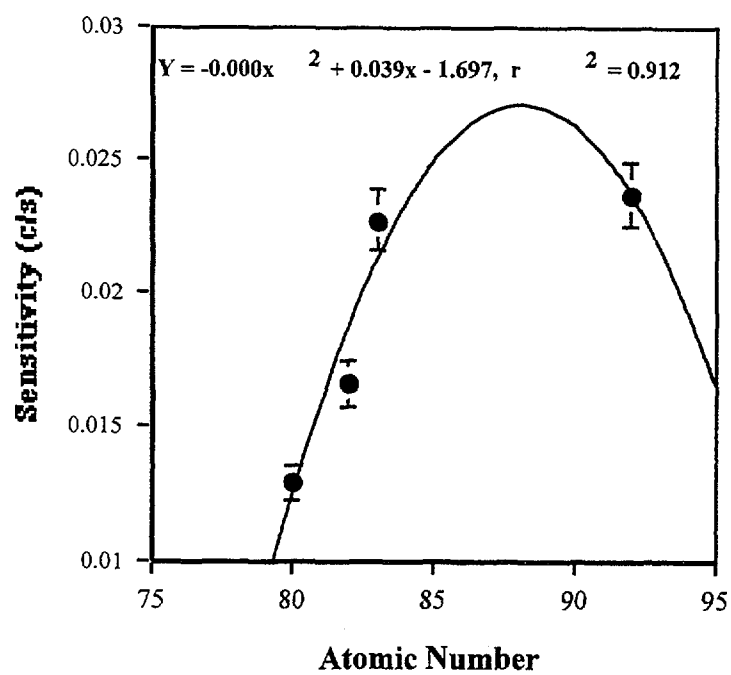


Fig. 19 Elemental Sensitivity Curve

4.4.2 Discussion

Results of mercury level measurements and analysis showed that the cosmetic cream "Madonna"(green) had the highest level ($\mu\text{g/g}$) of mercury - 29000 ± 2800 followed by "Madonna" (red) cream with 18000 ± 1700 . Significant differences($p < 0.001$) in the analytical results for "Madonna" (red), "Pimplex" and "Shirley"(original) were observed for the samples bought March and September, 1995. The creams, "Shirley" (new), "Dermovate" and "Topshirley", registered values below the detection limit ($3 \mu\text{g/g}$).

Two significant findings of this study is that mercury is present in some of the beauty products being sold in Kenya. This confirms previous findings which reported levels of mercury above $1 \mu\text{g/g}$ [Wandiga and Jumba, 1982]. Secondly, the level of mercury is not constant in different batches of some products bought during the sampling periods. For example, the mercury levels($\mu\text{g/g}$) during the month of March 1995 for "Madonna"(red) was 16080 ± 1030 ($n=5$); "Pimplex" cream ($n=5$) had 4350 ± 290 while "Shirley"(original) had 18090 ± 890 ($n=5$). For the month of September 1995, the mercury levels ($\mu\text{g/g}$) were: 20900 ± 1400 ($n=5$), 9644 ± 630 ($n=5$) and 10895 ± 690 ($n=5$) respectively. The highest variation (121.7%) was for "Pimplex" cream. This has the implication on the quality control during manufacture of these products and it is possible that some products could be on sale with even higher levels of mercury than those shown in this work.

Mercury levels in some of the products analysed were above the World Health Organization (WHO) limit of $5 \mu\text{g/L}$ in human blood [WHO, 1996]. Although the levels of mercury absorbed through the skin will usually be less than the levels in the samples analysed, the health implications on the uses of some of these products need to be investigated further. This is especially with the objective of tracing the causes of the presence of mercury in nails and hair [IAEA, 1978] plus renal problems and hypertension, reported previously and attributed to heavy metals especially among the youth in this country [Kinyua et al., 1990b]. In their study involving African women in Kenya [Barr et al., 1972] attributed damaged kidneys to the effect of mercury present in the skin lightener creams used by the women. However, previous studies [Kinuthia et al., 1978] observed that there was no single etiological factor found to be of major significance in the causation of nephrotic syndrome in Nairobi. The latter authors suggested the presence of a chemical pattern of nephrotic syndrome which co-existed with haematuria, azotemia and hypertension.

The major risks to human health arise from the neurotoxic effects of mercury in adults [Bakir et al., 1973] and its toxicity to the foetus if women are exposed to methyl mercury during pregnancy [Cox et al., 1989]. Since the form of mercury present in these beauty creams is largely organic [Jumba, 1996], there is need for the local authorities to implement stringent measures to curb the sale of these products. This is more so especially when the level of mercury appear to have increased tremendously in comparison to those reported in a previous survey [Wandiga and Jumba, 1982]. Organic mercury has greater affinity for the brain, and in particular, posterior cortex as well as adipose tissue beneath the skin [WHO, 1996]. The technique developed above can be utilized for fast and regular monitoring and has the added advantage of permitting multi-elemental analysis. Other well known chemical analytical techniques take too long due to lengthy sample preparation procedures before analysis, and also require expensive and toxic reagents.

4.5 Nairobi Industrial Effluents [Kinyua, 1997]

Table 15 Results of Kamiti River Analysis (ppb unless otherwise stated)

Parameter	Upstream		Downstream	
BOD	7 mg/L		20 mg/L	
COD	28 mg/L		112 mg/L	
S	1651 ± 251	1852 ± 497	3186 ± 335	3094 ± 267
Cl	6652 ± 275	5417 ± 398	4430 ± 229	5593 ± 161
K	12826 ± 253	11246 ± 312	9406 ± 201	10227 ± 158
Ca	10000 ± 15	10099 ± 150	15533 ± 129	16332 ± 136
Ti	155 ± 15	236 ± 23	159 ± 15	119 ± 10
Cr	< 23	< 37	34 ± 10	< 23
Mn	127 ± 12	143 ± 19	687 ± 15	550 ± 12
Fe	1590 ± 30	2181 ± 32	3279 ± 27	2748 ± 25
Cu	40 ± 10	< 48	< 19	< 16
Zn	24 ± 7 ppb	41 ± 11	25 ± 6	23 ± 6
As	< 34	< 56	< 32	< 26
Br	42 ± 13	61 ± 20	42 ± 11	104 ± 8
Rb	< 32	< 60	< 30	< 26
Sr	91 ± 13	103 ± 25	52 ± 15	89 ± 9
Pb	< 81	< 137	< 78	< 90

CONCLUSION

The concentration of SPM varied from 16 to 83 mg/m³, which falls below WHO 24 hour guidelines of 60 - 90 mg/m³ [WHO, 1987]. However, these levels are higher than previous data (16-60 µg/m³) [Gatebe et al., 1996] from a semi-urban site. The highest concentration of lead(Pb) observed during the period of study was 1.05 mg/m³ from the 0.4 µm filter. This value falls very close to the maximum WHO guidelines of 0.5 - 1.5 mg/m³. The equivalent value for 8 µm filter was 0.76 µg/m³ and is also higher than our previous semi-urban data. The concentration of potassium, calcium and iron varied from 0.2 - 2 µg/m³, with calcium registering a higher level than Fe and K over the entire period. Zinc levels remained high throughout the sampling period varying from 1.0 - 8.0 µg/m³. This implies some presence of some industry(ies) having some zinc emissions. In general, most the elements showed higher concentrations than those levels previously recorded at the semi-urban site.

The results of analysis of the effluents from the River Nyando showed that waste from the factories was certainly affecting the water quality of the river. High levels of sulphur (0.9 - 439 µg/ml) were registered at a waste treatment pond in the factory. The occurrence of these high levels during some sampling visits, suggests some random release of industrial wastes into the river. Other parameters affected by the industrial wastes included the conductivity, salinity and BOD. This calls on the authorities to initiate some strident monitoring of industrial wastes.

Construction activities and utility of unpaved roads in the area around the Voucher Processing Centre showed that these activities did contribute to increased dust particles in the workplace. Other air polluting activities include, industrial and traffic emissions [Gatebe et al., 1996].

There was also no significant reductions in the levels of heavy metals; iron (Fe), zirconium(Zr) and zinc(Zn) for samples collected from the Air Conditioner room and those from the Server room. This implied poor filtration of the air. Carbon and sulphur in the samples analysed seemed to be of the same origin. It was therefore concluded that the air filtration system in the premises was not efficient due to first, the room entrances and exits being not properly constructed so as not to allow the dust inside. Secondly, the openings on the ground floor for the cable installations were not properly sealed against the dust. It was therefore recommended that a closed/or open-loop air filtration system for the premises be installed. This system is capable of filtering out air particles sizes less than 10µm or less depending on the filter membrane installed. Finally, it was recommended that some dialogue and negotiations on the possible ways and means to reduce the particulate matter in air by way of clean production practices be initiated between the bank, the neighbouring firms and relevant authorities.

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Fig. 7 Variation of SPM for 8 μ m and 0.4 μ m Filters

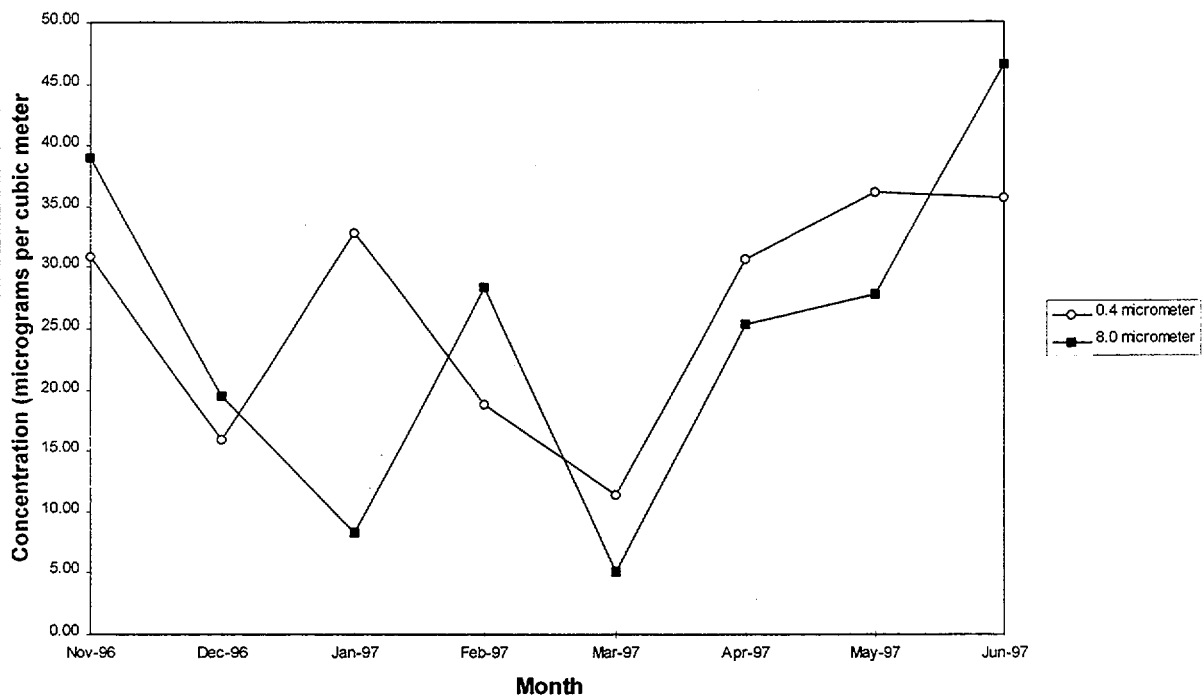


Fig. 8 Variation of Zn, Cu and Mn for 8 μ m Filter

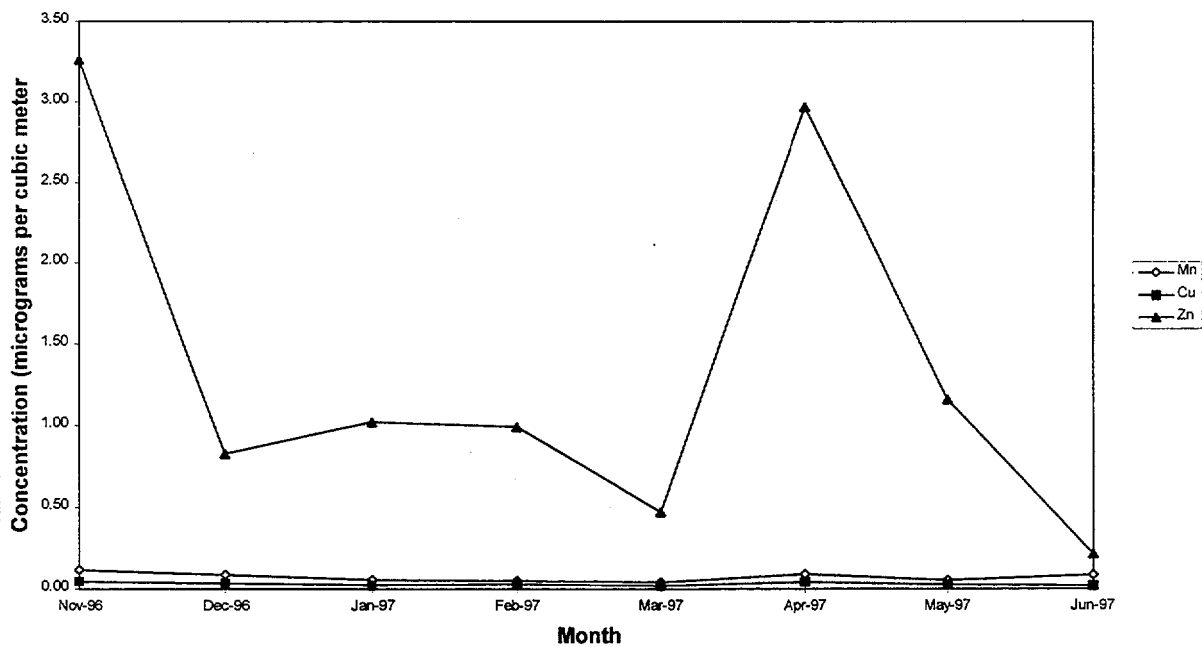


Fig. 9 Variation of Cu and Mn for 8 μ m Filter

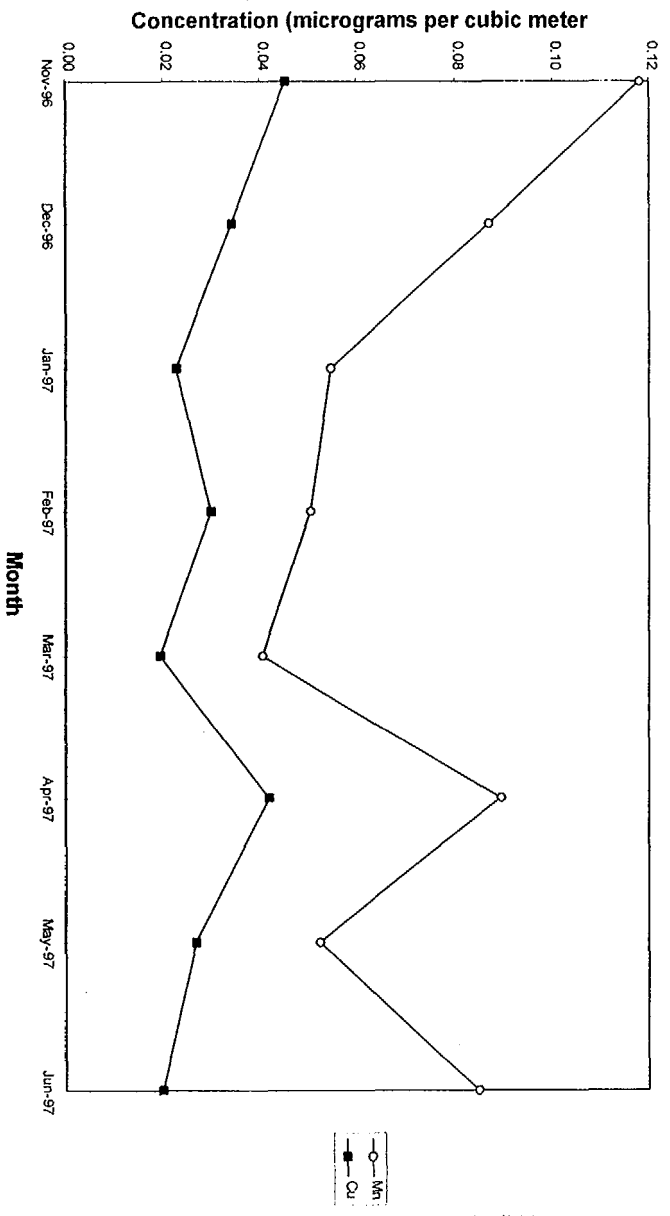


Fig. 10 Variation of Mn, Cu and Zn for 0.4 μ m Filter

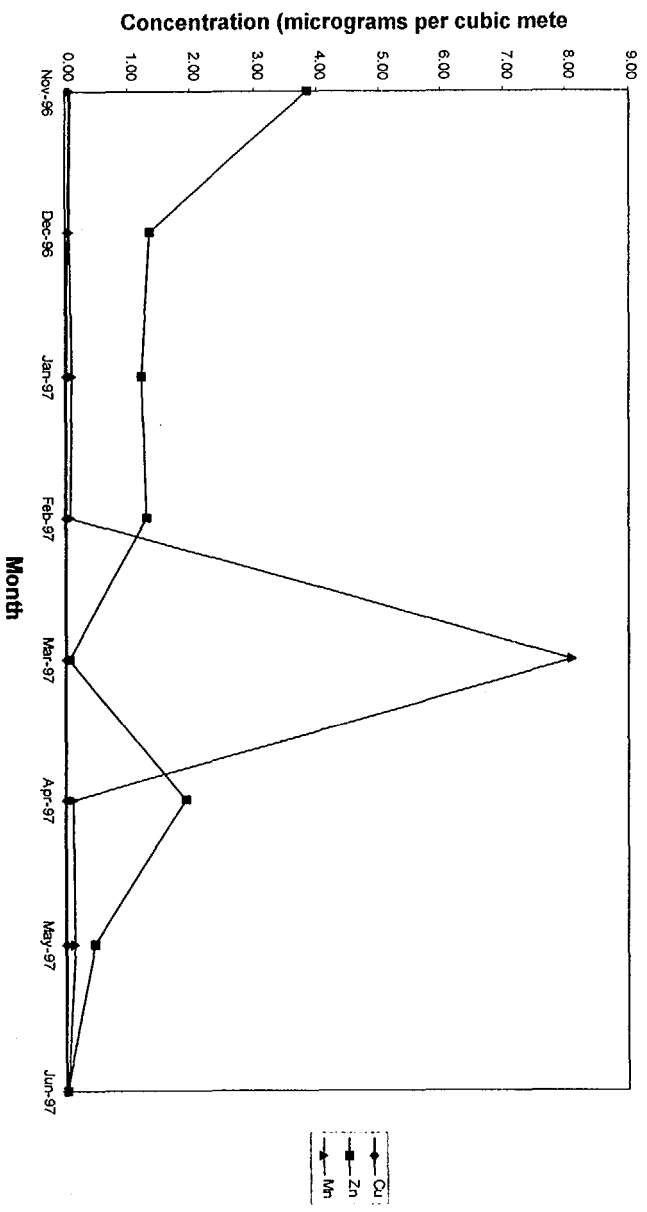


Fig. 11 Variation of K, Ca, and Fe for 8 μ m Filter

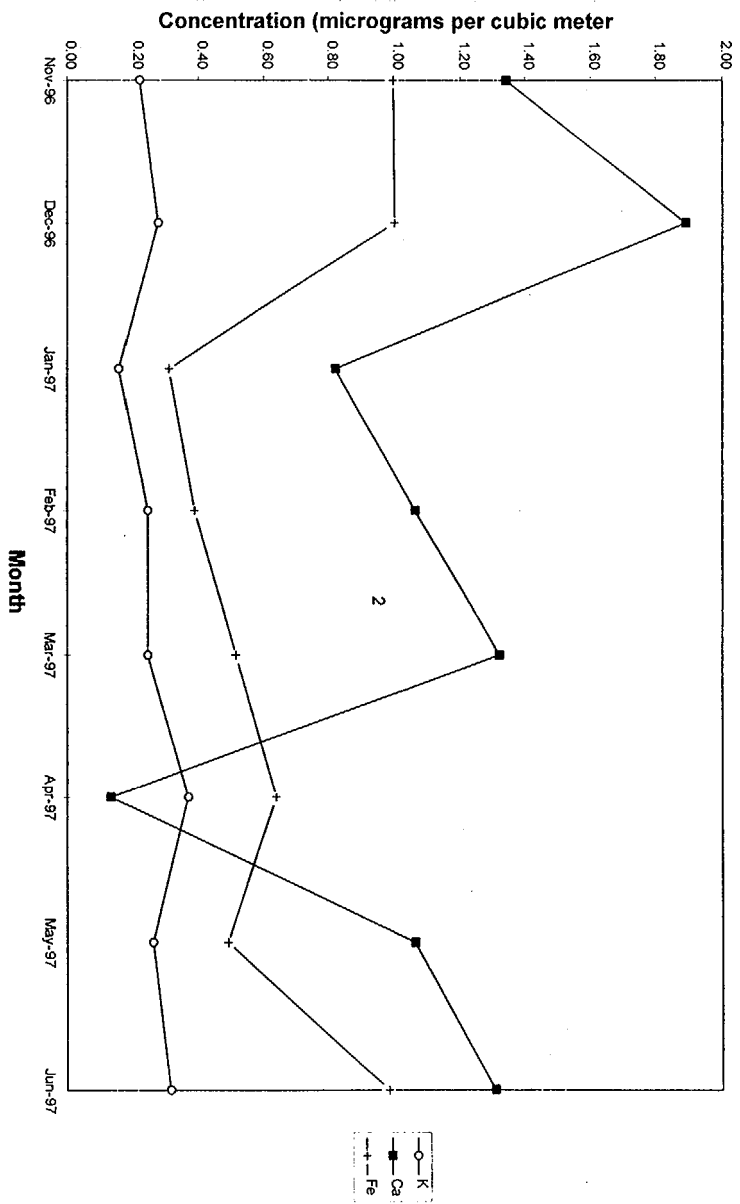


Fig. 12 Variation of K, Ca and Fe for 0.4 μ m Filter

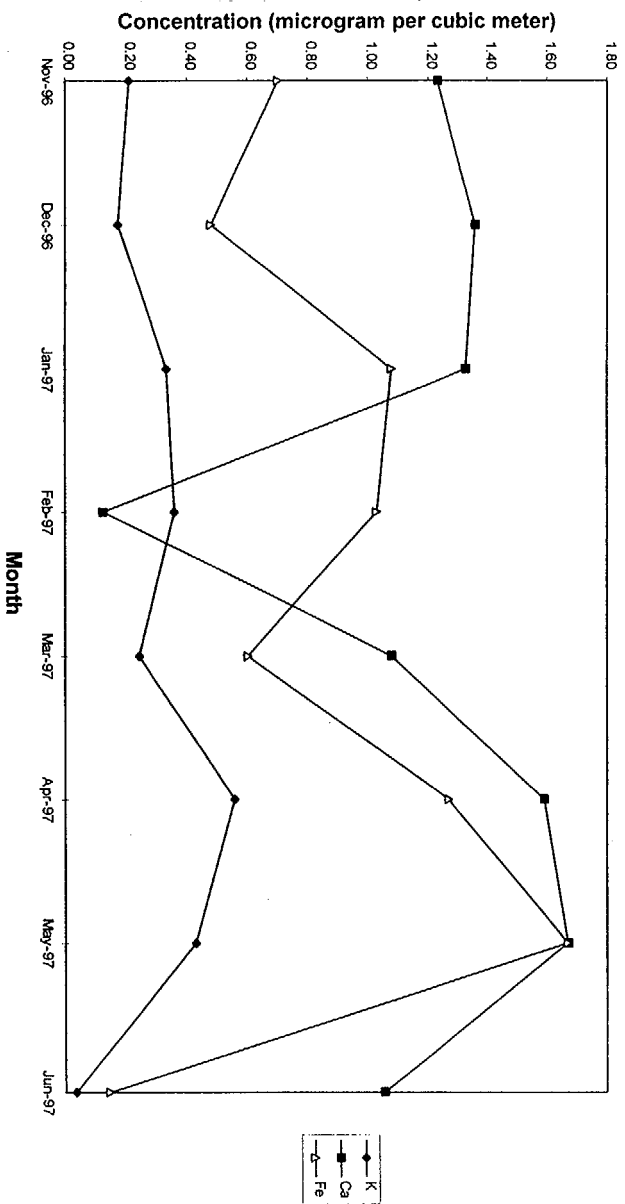


Fig. 13 Variation of Br and Pb for 8 μ m Filter

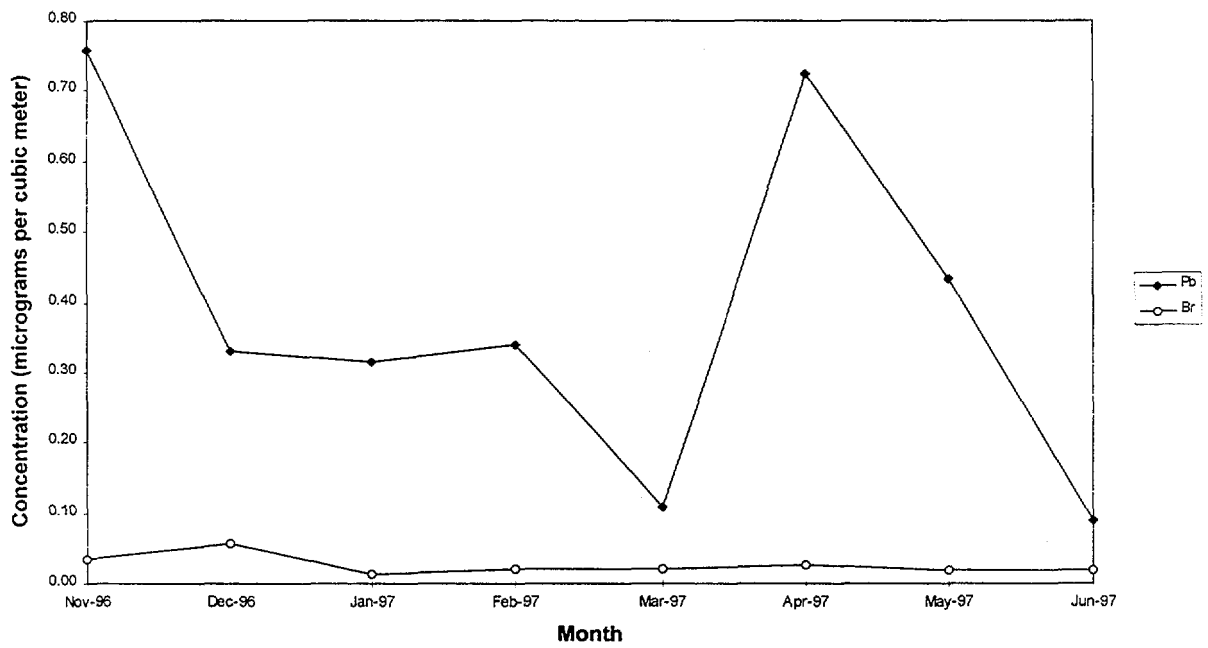
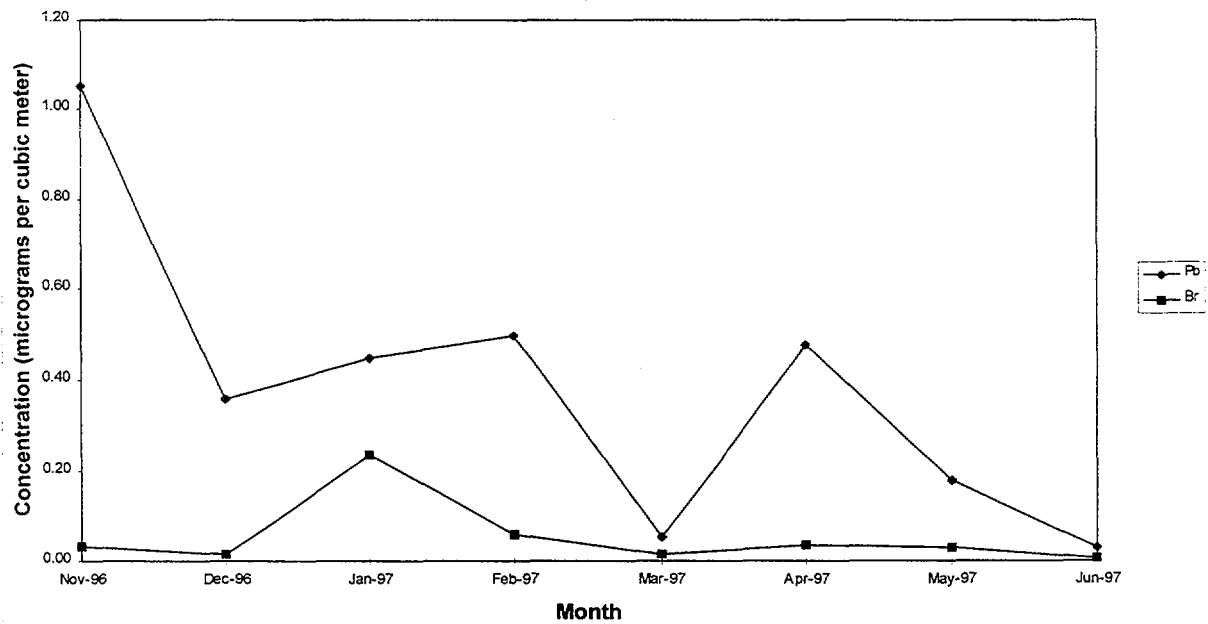


Fig. 14 Variation of Br and Pb for 0.4 μ m Filter





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Particulate Matter and Health - from Air to Human Lungs

RESEARCH TEAM

ITN - Physics

E.N. 10
2685 Sacavém
PORTUGAL
Tel: + 351-1-955 00 21
Fax: + 351-1-994 15 25
email (for correspondence): murmur@itn1.itn.pt

Teresa Pinheiro
Luís Cerqueira Alves
Miguel Reis
Rute Pinheiro

ITN – Chemistry

Maria do Carmo Freitas
Isabel Dionísio

Stª Maria Hospital

Hospital de Santa Maria
Serviço de Pneumologia
Av. Prof. Egas Moniz
1700 Lisboa
PORTUGAL
Tel: + 351-1-796 67 39
Fax: 351-1-797 29 88

António Bugalho de Almeida
Dolores Moniz
Emília Alvarez
Paula Monteiro

Abstract

The aim of this project is to search for respiratory system particular aggressors to which workers are submitted in their labouring activity. The work plan under the current IAEA contract comprise a prospective study to identify particulate matter deposited in the human respiratory ducts and lung tissue and workers respiratory health status survey at a steel plant, *Siderurgia Nacional* (SN). So far, the selection of areas of interest at SN, workers exposed, airborne particulate monitoring sites according to the periodicity of labouring cycles, and the beginning of workers medical survey have been achieved and/or initiated. The SN selected area, where steel is processed and steel casting is achieved, involve approximately 80 workers, most of them working at that location for more than 15 years. Blood elemental content data determined by PIXE and INAA and a preliminary health status evaluation from 32 of the 80 workers included in this survey are presented and discussed.

1. Introduction

The awareness of environment degradation and of indoor pollution in a way that may influence health has increasingly been attested by several epidemiological and toxicological studies [1-4]. However, despite the considerable large amount of data on air constituents that has been gathered in the past decades, the verified levels of pollutants are not always compatible with the magnitude of respiratory complains. Actual concern on influence of particulate matter size in the respiratory health and on restricted milieus arose, among other reasons, from the awareness that dispersion and air recycling in confined places are less efficient than in natural conditions [4]. Therefore, the indoor exposure dose of an individual may be considerably higher and probably more hazardous than in a natural environment. Thus, scientific evaluation of the links between air pollution and respiratory symptoms seem to be incomplete.

Some metals have been pointed out to be toxic to cells and carcinogenic, as V, Cr, Co, Ni, Cd, and Pb. These elements are often associated with the particulate matter fraction of inhaled air constituents [3-6]. Also, asbestos and typical indoor pathogens as dust mites are known to increase respiratory responsiveness and prevalence of sensitisation. Individual exposure to such agents, usually related with professional activity, may lead to interstitial lung diseases and to the progression of lung fibrosis [2,7]. Lately, some organic constituents of the environmental tobacco smoke are being connected directly with cancer. Aside all knowledge acquired, how particulate matter interact, how and where it deposits in the human respiratory ducts are problems that have been only approached by theoretical models [8].

The working environment monitoring and workers respiratory health control is far from being routinely performed in many Portuguese industries. Even in those, where the generation of dust and gases is significant, as the case of the steel industry, Siderurgia Nacional (SN), data on air quality parameters are scarce. Also, the workers medical exams performed periodically by the company physicians do not account for respiratory health monitoring. Therefore, statistic data on the harmful effects of airborne particulate in human beings inferred through affections or complains of workers exposed have not been regularly produced.

In the particular case of Portugal, some epidemiological surveys at industrial areas have been carried out since 1972. From 1974 to 1980, 3359 steel industry workers and 400 cement industry workers have been studied aiming at the evaluation of their respiratory health. It was then observed a high incidence of upper respiratory system affections, although lung diseases had low occurrence [9,10]. Also, for cement industry workers the duration of exposure was found to be related with the lung capacity function [10].

On the other hand, an evaluation of airborne suspended matter at several working places of the steel plant SN took place in 1988. The objectives were then, to initiate a survey to establish human exposure, although the project was not accomplished. However, the airborne particulate matter elemental characterisation have been performed since 1993 (some projects under the IAEA co-operation programmes) both for rural and urban areas, that include the industrial belt where SN is located.

More recently, collaboration with medical teams, permitted to start a prospective study to identify particulate matter deposited at respiratory ducts and to draw up a reference data set for healthy individuals [11]. The increase of constitutive and exogenous elements data basis for the human respiratory system as well as a micro-distribution approach of elements in the tissues, are objectives to be achieved in a near future, in collaboration with the Portuguese TXRF group (INETI) and the Oxford

Nuclear Microprobe group (Oxford, England). The need to assess this information may be crucial to the understanding of sensitiveness and response of the respiratory system to a specific aggressor. Also, the recognition of specific particles of atmospheric origin in the human respiratory system may give information about its preferential size and elemental composition as well as the deposition local. Therefore, health effects of the inhaled particulate matter, in specific environments as working places may be foreseen. Moreover, incentives to the environmental health research will eventually permit the establishment of more adequate air quality standards for indoor and outdoor environments.

2. Methods

2.1. Worker's Medical Inspection

The lung function evaluation was performed with a Vitalograph Compact II spirometer equipment that enables the determination of flow volume curves. The basal values were registered before a non-specific bronchial provocation test was done, using metacholine, to determine an eventual bronchial hyper-reactivity.

2.2. Blood Samples Collection and Preparation Procedures

Blood for elemental analysis purposes was drawn to polycarbonate centrifuge tubes using standard methods [12] to avoid contamination. All containers were previously thoroughly cleaned with analytical grade nitric acid and serum separated from the packed blood cells (PBC) fraction by centrifuging with 10000 rpm during 30 min at 4°C. All samples were freeze-dried and stored at -30°C. The wet and dry weight were determined for both blood fractions. Serum and PBC sub-samples to be irradiated for Neutron Activation Analysis purposes were separated to special polyethylene containers.

The samples to be analysed by PIXE were then subjected to an acid digestion procedure with Suprapure® nitric acid and hydrogen peroxide, together with Y as an internal standard in closed Teflon™ vessels (Parr® Bombs for microwave digestion). A commercial microwave oven was employed for sample digestion purposes using 300W power during 3min. Targets for PIXE analysis were produced by pipetting 10 µl of the resulting solution on to a 1.5 µm thick polycarbonate film previously washed with suprapure® nitric acid to make it hydrophilic. At least three targets are analysed for each sample.

2.3. PIXE and INAA Techniques

For all blood samples collected elemental analysis were carried out by PIXE. Some of these samples were also analysed by INAA technique.

The PIXE experimental set-up is installed at the ITN 3 MV Van de Graaff accelerator. The samples were irradiated with a 2.4 MeV proton beam under vacuum keeping the current density at the target below 250 nA.cm⁻². X-rays were detected by a Link Si(Li) detector, positioned at an angle of 110° relative to the beam direction, in front of a chamber window of 6.3µm Mylar™. To absorb the low energy radiation originating from the matrix and minor elements of the sample, an absorber of 350 µm Mylar™ was used between the detector and the chamber. The PIXE spectra were analysed by means of a non-linear least-squares fitting program AXIL [13] and the concentration calculations were performed with the DATPIXE program [14].

The INAA experiments were performed at the ITN Portuguese Research Reactor – RPI. The homogenised powdered serum and PBC (approximately 100 to 200 mg) were kept in a small container and irradiated. Short irradiation took place at the RPI pneumatic system with thermal neutron flux of $2.8 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$. Longer irradiation of 5h was carried out in the core grid with typical neutron flux $1.2 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$. The *k₀-method* [15] was applied to elemental quantification purposes; the 0.1% Au-Al wire was used as comparator. For the gamma measurement a hyperpure germanium detector (1.76 keV resolution at 1.33 MeV) was used. The spectra were fitted with SEQAL computer code and elemental concentrations were calculated with SOLANG and SINGCOMP programs.

3. Results

The SN selected area, where steel is processed and steel casting is achieved, involve approximately 80 workers. The sector is a confined area so, the permanence of airborne particulate matter at that working area may be larger, despite the existence of ventilator devices. Consequently, workers may be more continuously exposed to dust as long as a time scale is concerned.

The blood elemental contents were assessed for 32 workers by PIXE and for 12 of these by INAA. The PIXE technique permitted the determination of 9 elements in blood, i.e., K, Ca, Fe, Cu, Zn, Se, Rb and Pb. The available INAA results are relative to 8 elements, i.e., Mg, Na, Al, Cl, K, Mn, Br and Mo. In Table 1 the elemental contents determined by PIXE are listed, and compared with a Portuguese data base obtained for an urban healthy population [16] that will be taken as control values. Reference data set was found to be comparable with literature reported values [12,16].

A significant concentration decrease was found for Zn and Se in serum and K, Fe and Se in PBC. On the other hand an increase of K concentration in serum is verified (that may derive from incomplete serum and PBC fractions separation) while Ca is enhanced in PBC fraction. The Se concentration values obtained are close to PIXE detection limit (approximately 0.4 µg/g). Se average values are based on 28 individuals for serum samples and only 10 individuals for PBC samples.

Table 1 - Mean elemental concentrations and associated standard deviations ($\bar{x} \pm \text{st}$) in $\mu\text{g.g}^{-1}$ dry weight based on N individuals and wet-to-dry weight ratio (RF) for serum and packed blood cells. Reference values listed are relative to a healthy population not directly exposed [16].

	Serum (N=32)	Serum Reference Values (N=27)	PBC N=32	PBC Reference Values (N=27)
	$\bar{x} \pm \text{st}$	$\bar{x} \pm \text{st}$	$\bar{x} \pm \text{st}$	$\bar{x} \pm \text{st}$
K	4473 $\pm$ 2212 *	2100 $\pm$ 423	8740 $\pm$ 1460 *	10820 $\pm$ 750
Ca	665 $\pm$ 374 *	1149 $\pm$ 129	202 $\pm$ 65 *	76 $\pm$ 26
Mn				0.77 $\pm$ 0.21
Fe	58 $\pm$ 38	50 $\pm$ 23	2845 $\pm$ 138 *	3085 $\pm$ 126
Cu	11.7 $\pm$ 3.0	13.3 $\pm$ 4.7	4.07 $\pm$ 0.87 *	2.38 $\pm$ 0.36
Zn	13.7 $\pm$ 3.2 *	9.6 $\pm$ 2.0	37 $\pm$ 6	34 $\pm$ 5
Se	0.59 $\pm$ 0.18 *	1.72 $\pm$ 0.26	0.4 $\pm$ 0.3 (*)	0.66 $\pm$ 0.11
Rb	8.6 $\pm$ 6.4 *	3.1 $\pm$ 1.0	15.2 $\pm$ 4.0	17.7 $\pm$ 2.9
Pb			0.95 $\pm$ 0.65	1.02 $\pm$ 0.03
FR	10.7 $\pm$ 1.3	12.6 $\pm$ 1.1	3.4 ^a $\pm$ 0.2	3.7 $\pm$ 0.4

* Significant difference for $p < 0.01$ in a Student t-test [17]

(*) Significant difference for a $0.05 < p < 0.1$ in a Student t-test [17]

^a N=19

Therefore, uncertainties on the Se determination by PIXE are likely the responsible for the deviation observed. The mean K, Ca, Fe and Zn values differences encountered with respect to the urban population, although significant for a $p < 0.01$ have large standard deviations that for most of the cases overlap with reference group average values. Therefore, more cases have probably to be analysed to decide about the significance of differences encountered.

Comparing INAA results with literature values or with the reference Portuguese group a steady decrease of K values is observed (Fig.1). Literature reported average value for serum K is $2000 \mu\text{g.g}^{-1}$ dry weight while in PBC, K contents have minimum values of $10000 \mu\text{g.g}^{-1}$ and does not exceed $14000 \mu\text{g.g}^{-1}$ [12,16]. For the apparent systematic deviation of K content, determined by INAA, the influence of sample preparation can not be invoked.

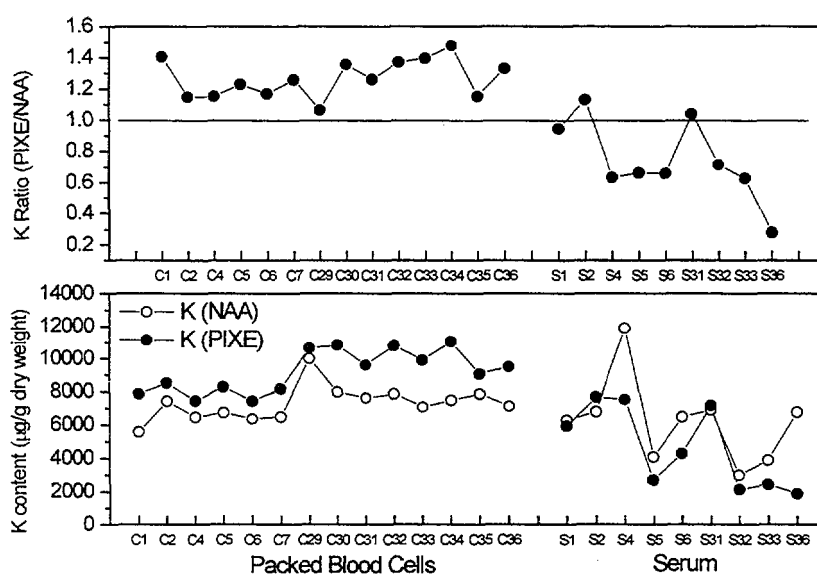


Fig. 1 - Comparison of K contents in packed blood cells and serum samples determined by PIXE and INAA.

Concerning the worker's health status evaluation, results are still not conclusive. As can be observed in Fig. 2, the number of years of exposure, smoking habits and respiratory symptoms are not clearly associated. So far, 18% of individuals observed have an apparent respiratory affection (lung function tests are not still completed evaluated neither thoracic radiographs). Also, if elemental contents are evaluated with respect to smoking habits, any significant differences are found between the three groups established: non-smoking, smoking and ex-smoking persons. The results obtained for serum and PBC are listed in Tables 2 and 3.

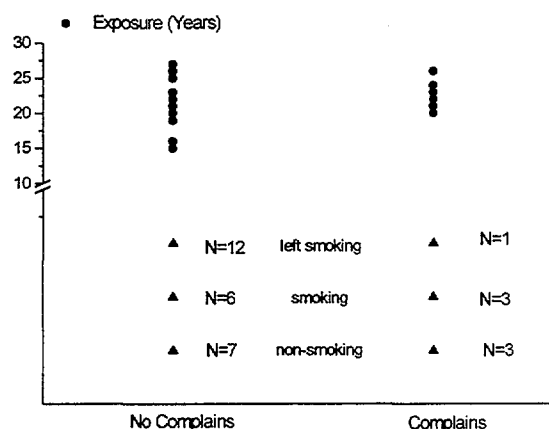


Fig.2 – Respiratory complains with respect to smoking habits and total number of years of exposure.

Table 2 - Elemental contents ($\bar{x} \pm st$) in $\mu\text{g.g}^{-1}$ dry weight in serum. The groups were established according to smoking habits (1 for non-smoking, 2 for smoking and 3 for ex-smoking). The elemental contents determined by INAA are indicated in table.

	Group 1		N	Group 2		N	Group 3		N
	$\bar{x}$	$\pm st$		$\bar{x}$	$\pm st$		$\bar{x}$	$\pm st$	
Exposure (years)	21.6	± 4.0	9	21.1	± 3.5	10	21.4	± 4.0	13
K	3300	± 2041	9	4982	± 2000	10	4892	± 2332	13
Ca	809	± 273	9	640	± 500	10	586	± 321	13
Fe	42	± 20	9	70	± 48	10	60	± 38	13
Cu	13	± 3	9	11.7	± 2.6	10	12	± 1	13
Zn	13	± 2	9	14.3	± 4.9	10	14	± 2	13
Se	0.65	± 0.18	9	0.47	± 0.22	10	0.49	± 0.26	13
Rb	6	± 3	9	7	± 5	10	11	± 7	13
Ni	2.4		9	0.71	± 0.12	10	0.76	± 0.26	13
Sr	2.6		1	2.34	± 0.96	3	4.4	± 5.6	5
Na (INAA)	26500	± 1480	5	28225	± 1810	4	27175	± 2990	4
Al (INAA)	576		1						
Cl (INAA)	27780	± 3380	5	31250	± 1723	4	30255	± 3350	4
K (INAA)	5450	± 1910	2	8530	± 2920	3	4930	± 1740	4
Br (INAA)	16	± 2	3	27		1	24.5		1

Table 3 - Elemental contents ($\bar{x} \pm st$) in $\mu\text{g.g}^{-1}$ dry weight in packed blood cells. The groups established refer to smoking habits (1 for non-smoking, 2 for smoking and 3 for ex-smoking habits). The elemental contents determined by INAA are indicated in table.

	Group 1				Group 2				Group 3			
	x	±	st	N	x	±	st	N	x	±	st	N
Exposure (years)	21.6	±	4.0	9	21.1	±	3.5	10	21.4	±	4.0	13
K	9700	±	1240	9	8380	±	1320	10	8350	±	1480	13
Ca	160	±	62	9	220	±	19	10	216	±	80	13
Fe	2830	±	130	9	2840	±	100	10	2860	±	170	13
Ni	1.7	±	0.9	9	1.6	±	1.1	10	1.9	±	1.1	9
Cu	4.2	±	0.7	9	4.3	±	1.2	10	3.8	±	0.7	13
Zn	39	±	8	9	36	±	6	10	36	±	5	13
Se	<MDL				<MDL				0.24	±	0.32	13
Rb	16	±	5	9	15	±	4	9	15	±	4	13
Sr	2.5			1	<MDL				1.4			1
Pb	0.95	±	0.79	6	0.87	±	0.79	5	1.1	±	0.3	4
Mg (INAA)	131	±	51	3	159	±	14	2	143	±	53	2
Na (INAA)	2950	±	490	5	2880	±	620	4	2670	±	707	5
Cl (INAA)	6860	±	714	5	6850	±	320	4	6500	±	785	5
K (INAA)	7210	±	570	5	7810	±	1530	4	6980	±	1010	5
Mn (INAA)	0.26	±	0.01	2					0.83			1
Br (INAA)	5.12	±	1.70	4	5.9	±	0.8	3	5.4	±	0.8	4
Mo (INAA)	0.50	±	0.23	2	0.53			1	0.74			1

If cases and/or variables in serum are examined for their similarity using a statistical procedure called cluster analysis [17], the individuals that had respiratory complains, i.e. 3, 9, 17, 19, 20, 21 and 23, are aggregated in the same group, as can be observed in Fig. 3. The variables used in the statistical analysis were the elements determined by PIXE, as referred above, total number of working years at the SN steel casting sector (variable "Yexp"), smoking habits (variable "SmHa") and occurrence of complains (variable "Complain"). On the other hand, for PBC samples the separation of cases with positive symptoms is not evident. The major feature found for the PBC data set, is the separation of two large groups that identify individuals where Pb concentration is more elevated and individuals with lower Pb blood content.

The variables were also clustered to infer any common behaviour or identification of similar episodes, and the resulting dendrogram are displayed below the correspondent cases agglomeration in Fig. 3. It can then, be observed that for both serum and PBC data sets the occurrence of complains is consistently associated with the total working years.

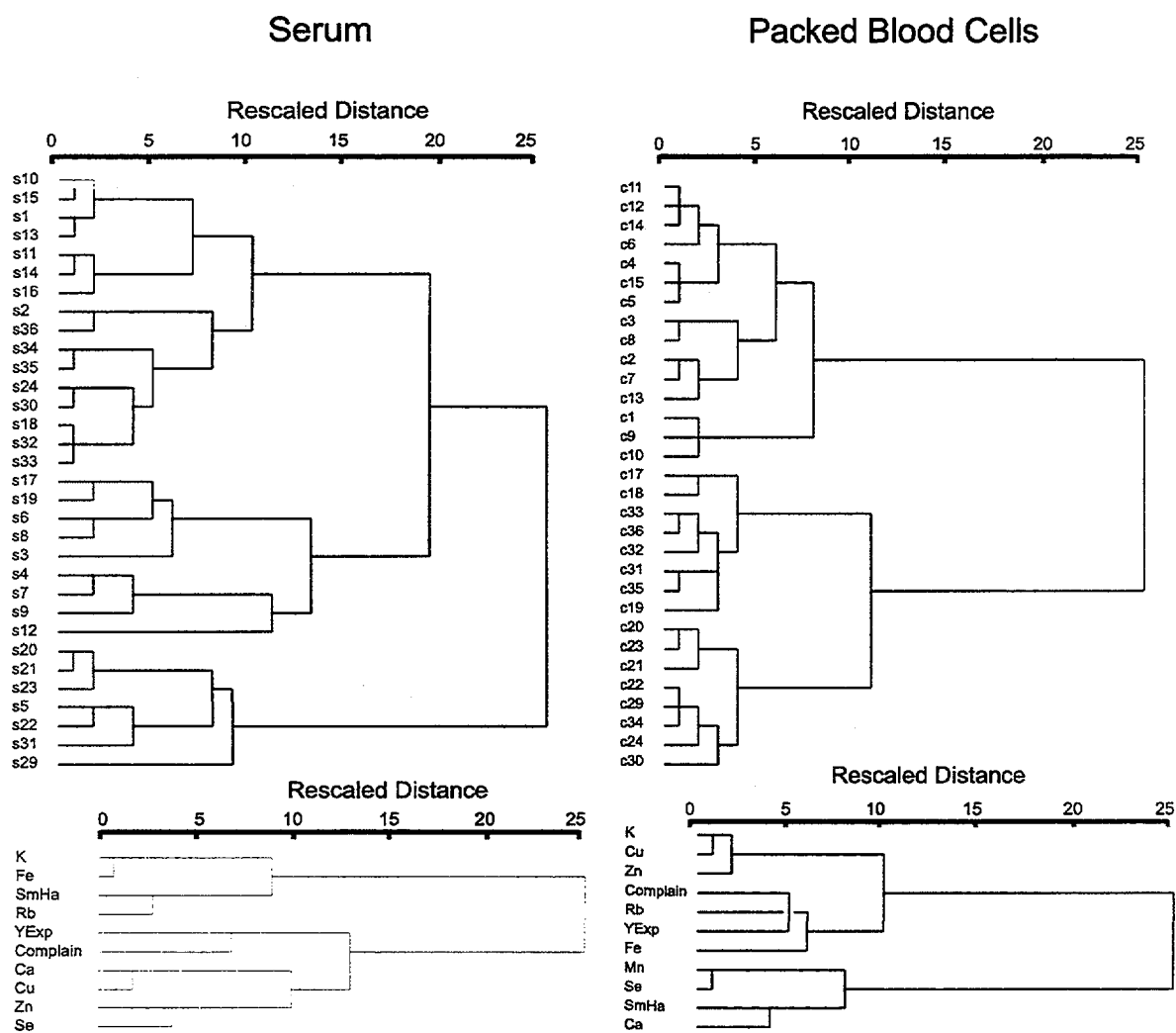


Fig. 3 – Dendrograms for Serum and PBC data sets. Both cases and variables are grouped. The Ward's method was used for the agglomeration procedure and the distance measurement obtained by the squared Euclidean distance method.

5. Plans for Future Work

The progression of the work plan, as presented in the research contract proposal submitted to the IAEA Co-ordinated Research Programme, will permit:

- the continuation of elemental analysis on samples already collected: blood and aerosol samples to check whether the elemental associations and alterations found in blood derive from exposure;
- to collect air particulate air samples repeatedly (not only the survey that is starting in October), that will allow to estimate indoor air quality and airborne particulate matter characterisation using both PIXE and INAA techniques;

- to continue medical examinations to workers exposed in order to infer and/or confirm any alteration that can be related to the working environment exposure;
- to gather data on respiratory system particulate matter deposition, through autopsy samples collected from healthy individuals and occasionally from individuals with respiratory affections due to professional activity (data is being collected since June 97 although elemental analysis had not yet been initiated). Samples will be analysed by PIXE and INAA whenever possible.
- Therefore, increasing data both from indoors airborne particulate and health status indicators (lung function response, blood exogenous elemental burden, etc.) will conduct to a better approach of risks to human respiratory health. Also, data gathered on a routine basis on air particulate matter elemental characterisation from an area comprising the Siderurgia Nacional and living area of individuals observed, will be useful to identify similar elemental combinations that may be found at the human respiratory system.

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Research Contract No. 9480/RO

**WORKPLACE MONITORING AND OCCUPATIONAL HEALTH STUDIES
AT THE CENTRE FOR PRODUCTION OF PHOSPHORUS MINERAL
FERTILIZERS, VOSKRESENSK (MOSCOW REGION, RUSSIA),
USING NUCLEAR AND RELATED ANALYTICAL TECHNIQUES**

Joint Institute for Nuclear Research, Dubna, Russia
Institute of Geology of the Academy of Sciences of Russia, Moscow

M.V. FRONTASYEVA

December 15, 1996

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M.V. FRONTASYEVA, A.V. GORBUNOV*, S.M. LYAPUNOV*, C. D. OPREA

Joint Institute for Nuclear Research, 141980 Dubna, Moscow Region, Russia

* Institute of Geology of RAS, Pyizhevskij per., 7, 109017 Moscow, Russia

ABSTRACT

This report contains the preliminary data obtained while monitoring the workplaces of the "Mineral Fertilizers" plant in Voskresensk (Moscow Region), one of the largest centres for producing phosphorus mineral fertilizers in Russia. Assessment of the present-day environmental situation for the main industrial premises of the plant is given. The most typical associations of element-pollutants in the shops of the plant were determined by means of XRF, AAS and NAA. The maximal pollution by dust particulates and the highest concentrations for Na, Ca, Sc, Cr, Fe, As, Sb, Sr, REE, and Th at the loading-unloading sites of the shops were revealed. Quite notable, but not exceeding the maximum permissible level, content of As was determined on the premises of the Central Laboratory of the plant. The total dust impact on the quality of the drinking water consumed at the plant and on the biosubstrates of the occupational staff (hair, nails) were examined. The level of trace element concentrations in the biosubstrates reflects the sustained and systematic impact of air pollutants in the working area of the plant on its occupational staff. Biochemical association of trace elements accumulated in employee hair fully correlates with the specific element content of the atmospheric aerosols. Data on the trace element content in nails is identical to that in the hair of the examined staff. Preliminary results of the REE distributions in employee teeth differ from those in the aerosol component of the air at the working sites. The same differentiation for REE is characteristic for employee hair, especially for Sm/Eu, obtained by means of radiochemical analysis. Due to the considerable emissions of fluorine in the technological process, the necessity of assessing the fluorine accumulation in the occupational staff is emphasized.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

Intensive production of phosphorus fertilizers requires a thorough investigation of the deterioration of the environment, including its pathological impact on occupational staff. Nuclear and related analytical techniques enable relationships to be established between the concentrations of elemental pollutants (Cr, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, Pb, (REE), Th, U, and other) in raw material, byproducts, humans and the workplace.

The goal of this project is to determine how man's biosubstrates can be used to follow the rate of pathological changes in the organism as it is exposed to intense technogenic environments.

As a rule, the degree of pollution of the environment is determined by studying the amount of sulfur and nitrogen compounds and fluorine in the air. In the early 1980s, specialists of the Institute of Mineralogy, Geochemistry and Crystallochemistry of RAS used emission spectrography to provisionally study of geochemistry of soils and snow around the "Mineral Fertilizers" plant in Voskresensk (Moscow region) and Apatity (Kola

Peninsula). This study revealed another, previously unknown, type of pollution: increased REE, zinc, and strontium [1]. The potential environmental hazard of phosphorus fertilizers and their byproduct is a well established fact now [2-5]. Investigation [1] stimulated further studies [6-8] in 1985-1989 by M.V. Frontasyeva, A.V. Gorbunov and B.A. Revich, the authors of the present IAEA project, using the more precise methods of X-ray fluorescence (XRF) and neutron activation analysis (NAA). At that time the task was to assess the eco-geochemical situation in the northern part of the town of Voskresensk (see Fig. 1). We studied the main anthropogenic streams blown into the air, which then fall back to the earth's surface (soil, snow), as well as their uptake into agricultural plants nearby and into local residents. The impact of technogenic flows on man's organism was examined by comparing the concentrations and associations of various elements in hair from relatively normal and impacted subjects [9].

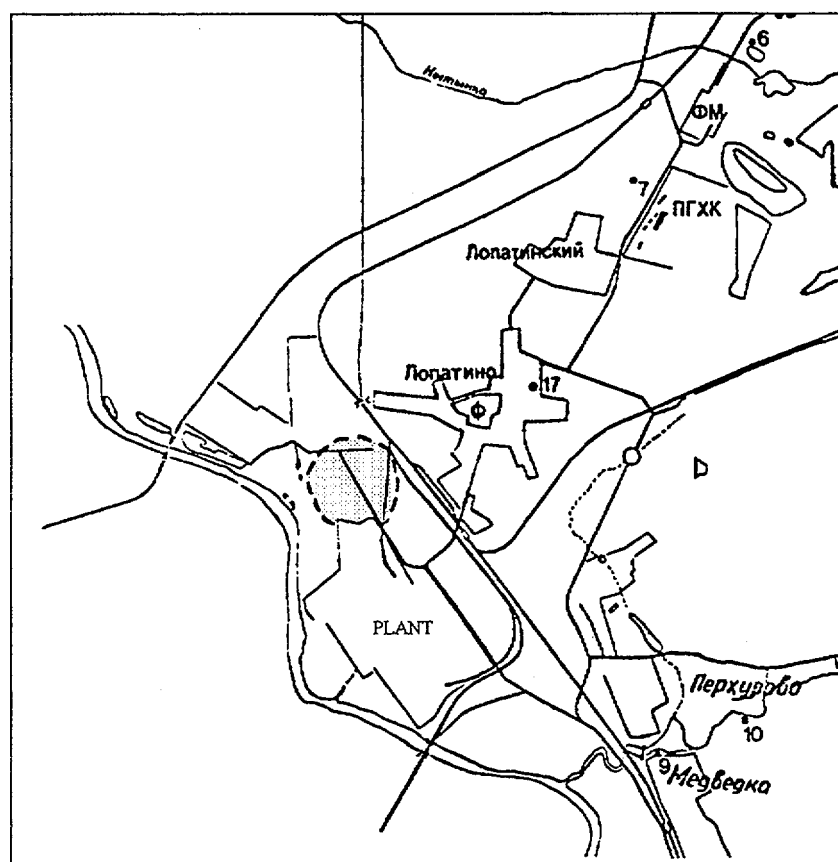


Fig. 1. The "Mineral Fertilizers" plant in Voskresensk.
The dashed area was examined in the previous studies [6-8].

From 1989 to 1993, the plant was rebuilt to more efficiently utilize phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 0.6\text{-}1.0\% \text{P}_2\text{O}_5$). As a result of the oleum sulphate extraction process (the most common one in the production of phosphorus fertilizer), approximately 5 t of phosphogypsum are precipitated per 1 t of final product (ammophos, or ammonium phosphate: 47-60% P_2O_5 , 11-13% N, 1-2% Ca). There are several ways of disposing of phosphogypsum: to use it as an agricultural meliorant, as a building material (tile, filling and binding components), etc. Practically all of the methods of phosphogypsum disposal were developed without taking into account the increase in

pollution levels caused by element-impurities in the phosphate raw material. For this and other objective reasons, the byproduct goods did not find a market, and the shop for reprocessing the main disposal waste (phosphogypsum) was shut down. The production of complex mineral fertilizers was shut down also, as well as the production of oleum phosphate in one of the shops, specifically, OPS-2. In addition, the technology of oleum sulfate extraction was changed. These activities must have altered the environmental situation in and around the plant, and, in turn, its effects on humans.

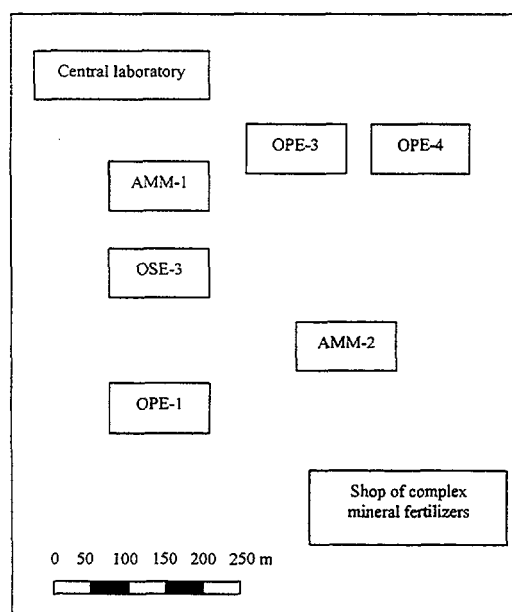
The present-day products of the "Mineral Fertilizers" plant in Voskresensk are summarized in **Table 1**.

Table 1

PRESENT-DAY PRODUCTION AND ELEMENT ASSOCIATIONS MOST TYPICAL FOR THE RELEVANT SHOPS OF THE "MINERAL FERTILIZERS" PLANT IN VOSKRESENSK

No	Type of production	Shop	Association of chemical elements
1	Ammonium phosphate fertilizers	AMM-1, AMM-2	Sr, Y, Bi, REE
2	Oleum phosphate extraction	OPS-1, OPS-3, OPS-4	Sr, Y, Mo, Zn, REE
3	Oleum sulphate extraction	OSE-3	Sr

Allocation of the main shops under consideration on the premises of the plant is shown in **Fig. 2**.



To clarify the present-day situation at the "Mineral Fertilizers" plant it was necessary to:

- determine the content and level of air pollution of the working areas and the drinking water;
- determine the normal and abnormal concentrations of elements in biosubstrates (hair, nails, bone tissue – teeth) of the occupational staff.

Fig. 2. "Mineral Fertilizers" plant premises.

2. METHODS

2.1 Sampling

The sampling strategy is based on the assumption that, at the workplace, the main sources of the technogenic impact on the human organism are the air of the workplace and drinking water consumed in the shops.

2.1.1. Environmental samples

Atmospheric aerosols and pollution streams (dust) blown into the air and which then fell back around were collected in the workplace. To collect aerosols on filters (AFA-XA-20, Russia), the aspirator (model 822 and AC-1, Russia) was used continuously during the working time (6-8 hours) [10]. Dust samples were collected directly in the workplace from an area 10 sq. cm by means of a fur brush, taking into consideration the whole area examined and its dustiness. Tap water was collected from the drinking fountains at the shops in clean plastic bottles 1.5 liter in volume. As the central water supply system provides the shops with fresh water, water samples were collected in only two shops (OSE-3 and OPE-3) and were conserved as required elsewhere [11].

To estimate the most probable sources of the air pollution in the working area, samples of the main type of industrial raw material (apatite concentrate), the final product (ammophos), and its byproduct (phosphogypsum) were collected.

2.1.2 Human biosubstrates

Diagnostic samples of human biosubstrates were collected in all operating shops. The list of occupations and relevant shops are given in **Table 6**.

1) Collection of hair samples from the occupational staff was carried out in accordance with the scheme shown in **Fig. 3** [12] as adopted by the World Health Organization. Not less than 500 mg of hair for each sample was collected.

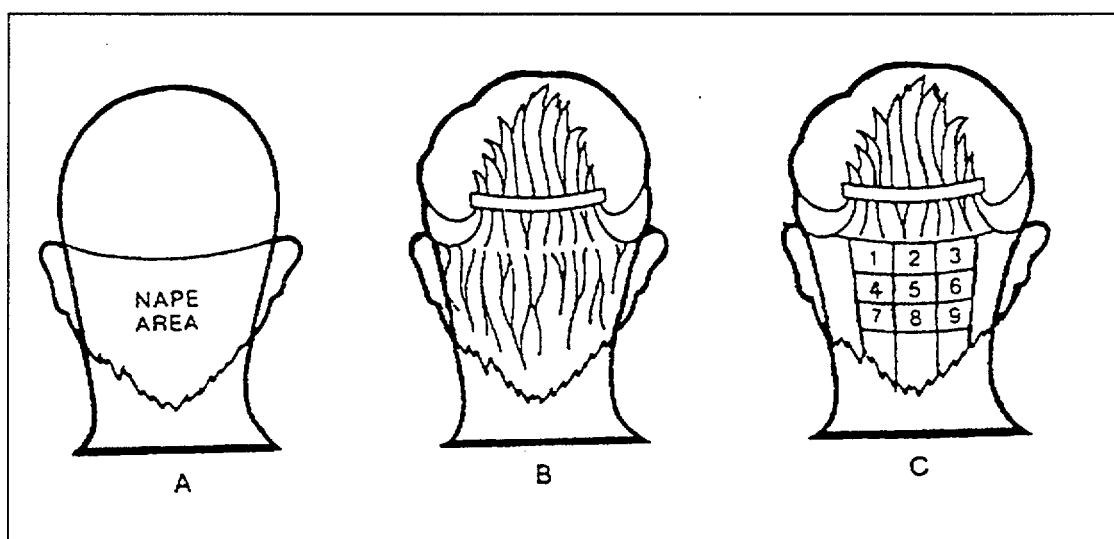


Fig. 3. Collecting hair samples.

- Locate a region on the scalp between the top of the ears and the nape of the neck (see figure A)
- Fasten the hair not to be cut out of the way with plastic clips (see figure B)
- Cut 10-20 strands of hair from 5-10 different sites in the occipital region of the scalp with stainless steel surgical scissors (see figure C). Save only the 5 cm of hair growing next to the scalp (if the hair is longer than 5 cm)

2) Simultaneously with the collection of the hair samples, nail samples were collected from some of the examined employees.

3) Samples of bone-tissue (teeth) were obtained from the stomatological medical clinic of the plant. These samples were not differentiated by shop or occupation.

Age, sex, the total length of service in the shop, and at the plant, was fixed in a protocol (see APPENDIX I). To avoid surface contamination prior to analysis of the biosubstrate samples the hair, nails, and teeth were subjected to a special cleaning procedure described elsewhere [13]. All of the collected samples were stored in hermetic zip-lock type plastic bags.

Thus, 23 samples of atmospheric aerosols, 15 samples of dust, 2 samples of drinking water, 3 technological samples, 36 samples of hair, 5 samples of nails and 5 samples of teeth were collected. The total number of samples subjected to analysis during the first year of the project was 89.

2.2 Analysis

The element concentrations of samples collected during the first year of the project were determined by means of NAA, XRF, and AAS.

The XRFA of the aerosol filters, dust, and technological samples for Ti, Mn, Cu, As, Rb, Sr, Y, Zr, Nb, Ba, Pb determination was carried out using a MECA-1044A (XR-500) analyzer (LINC SYSTEMS, Great Britain) with a pulsed X-ray tube and a silver target as a source of excitation. The detection energy resolution at the 5.9 keV K-line of Mn was 160 eV. A double-channel spectrometer XRF-WD (ARF-6, Russia) was also used [6, 14].

Heavy metals in the drinking water were determined by the method of preconcentration sorption filters with grafted chelate groups. The sorption filters were measured then by XRFA [15]. The rare-earth elements in the drinking water were determined in the salt residuals after evaporation by means of neutron activation analysis. Individual elements in the drinking water were determined with the atomic absorption spectrometer FAAS-3 (Germany) [14], the sample being placed directly into the flame (acetylene-air mixture) after preliminary sample preparation.

Neutron activation analysis of the biosubstrates, aerosol filters, dust and technological samples was used to determine Na, Ca, Sc, Cr, Fe, Co, Zn, As, Br, Cd, Sb, Ba, REE, Au, Hg, Th, and U. The analysis was performed at IBR-2 reactor in Dubna and at IRT research reactor at Moscow Technical University (MPhI) as described in [14]. The integral flux of epithermal neutrons was 10^{16} – 10^{17} neutron/cm². The temperature of the container with the samples during irradiation did not exceed 70 °C. The induced activity was measured with the using ORTEC γ -spectrometer of energy resolution 1.9 keV at the 1333 keV line of ⁶⁰Co.

3. RESULTS

The data on the trace element concentrations in the air of the premises of the plant and dust collected in the shops are given in **Table 2** and **Table 3**, respectively. The analysis showed that the maximum permissible levels for trace elements in the workplaces have never been exceeded. The maximum air pollution with airborne particulate matter as well as the maximum concentrations of Na, Ca, Cr, Fe, As, Sb, Sr, REE, and Th occur at

the loading-unloading sites. One should note relatively high, but not exceeding the maximum permissible, levels of As in the air of the Central Laboratory premises.

Table 4 presents the elemental content of mineral raw material (apatite concentrate), final product (ammophos), and industrial waste byproduct (phosphogypsum). It follows from this data that F, As, Sb, REE, Th, and U are of the highest potential hazard for the given environment.

The data obtained for the drinking water consumed at the plant (**Table 5**) do not exceed the relevant maximum permissible levels.

The information on occupations and shops of the examined personnel of the plant is given in **Table 6**. To study the environmental impact on the population health such diagnostic biosubstrates as blood, urine, hair and nails are most often used. Human hair are responsible for the release of chemical elements from the organism, the rate of this release through hair varies from $1 \cdot 10^{-3}$ to $1 \cdot 10^2$ μg per day [9]. Accumulation of trace elements in hair allows one to characterize the sustainable and systematic impact of pollutants, which is of special importance for our study.

The trace element concentrations in the hair of the occupational staff are given in **Table 7**. Biochemical association of trace elements accumulated in the hair fully correlate with the specific features of the content of atmospheric aerosols. For example, the results obtained allow the shop OPE-3 to be distinguished as a source of increased concentrations of Ca, Cr, Fe, As, REE, Th, and U. However, it is evident that for a reliable statistical analysis with account of shops, occupations, age, length of service, etc. the experimental material under consideration is insufficient.

The employee nails (**Table 8**) show the same identity with hair in accumulating the trace elements. However, there is always a possibility that nails are not cleaned enough from the surface contamination.

The results of the analysis of the bone tissue (teeth) of the occupational staff are presented in **Table 9**. The difference in the level of element concentrations in individual samples is quite substantial. Perhaps it could be explained by the presence or absence of the artificial dental prostheses in the mouth and by the material they are produced from. One should note the differential distribution of REE (Sm/Eu ratio) obtained from the radiochemical analysis.

4. CONCLUSIONS

1. The main chemical pollutants at the plant are F, Ca, As, Sb, REE, Th, and U, which is confirmed by the analysis of the atmospheric aerosols and the hair of the occupational staff. The main source of pollution is the raw material (apatite concentrate).

2. The drinking water consumed at the plant could not be considered as a source of the uptake of the above-mentioned elements into a human organism.

3. Due to atmochemical network the workplaces characterized by the increased level of trace element pollution in air are revealed.

4. The trace element content of the hair of the occupational staff reflects the pollution of the workplaces.

5 There is a hope that more thorough study of the trace element content of teeth could help to reveal the interrelation between the concentration of Ca on the one hand, and of F, Sr, and REE, on the other.

6. One should note that the further sampling of dust and nails is not reasonable.

5. PLANS FOR FUTURE WORK

For the logical completion of the present study, the following plan is suggested:

- To carry out an additional sampling of the atmospheric aerosols in the work places, as well as hair and teeth of the occupational staff, aimed at accumulating a reasonable amount of data for a reliable statistical interpretation of the results obtained.
- As fluorine is emitted in the production of phosphorus fertilizers causing *fluorosis* in the occupational health, we plan to determine the fluorine content in the air of the work places of the plant and in hair of the occupational staff.
- Since there are data on the substitution of Ca by Sr in bones, it would be interesting to examine such distribution in teeth by means of XRF and NAA.
- The noted selective differentiation of REE in biosubstrates (preferable accumulation of Eu and Ce in teeth and hair) could be thoroughly studied using radiochemical NAA.
- Correlation of the biochemical data obtained with the resulting health effects should be examined.

The detailed working plan is as follows:

Month 1-3

- Continuation and completion of NAA of hair, dust, industrial products, wastes, raw material.
- Data processing.
- Comparison with the previous data obtained during the first year of the project.

Month 4-6

- Collection of aerosols and biosubstrates for fluorine content.

Month 7-9

- NAA of aerosols and biosubstrates followed by radiochemical separation.

Month 10-12

- Statistical analysis of the results. Estimation of the sanitary-hygienic situation at the plant by comparing the elemental contamination of workplace and biosubstrates of occupational staff with the results of medical tests.
- Preparation of the annual report.

We plan to use the third year of the project (with a possible extension to 5 years) for repeating the workplace monitoring of the fertilizer plant and extending the study to the occupational staff and local residents of the phosphate ore open-cast mining enterprise, situated 3-7 km from the main plant.

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APPENDIX I

АНКЕТА №		2		РОССИЙСКАЯ АКАДЕМИЯ НАУК	
Фамилия		Имя		Отчество	
Сергиев		Анатолий		Константинович	
Год рождения		Домашний адрес			
1958		Тюменская 14-20			
Цех		Стаж работы в данном цеху			
ЭФК-3 (сладкая вода)		20 лет			
Специальность		Стаж работы на НПО "Минудобрения"			
слесарь		20 лет			
Номер пробы	ВОЛОСЫ	+	НОГТИ	+	

PROTOCOL No.		Russian Academy of Sciences	
Family name	First name	Patronymic name	
Date of birth	Home address		
Shop	Length of service in a given shop		
Occupation	Length of service at "Mineral Fertilizers" plant		
Type of sample	HAIR	NAILS	

**CO-ORDINATED RESEARCH PROGRAMME
ASSESSMENT OF LEVELS AND HEALTH-EFFECTS OF AIRBORNE
PARTICULATE MATTER IN MINING, METAL REFINING AND METAL
WORKING INDUSTRIES USING NUCLEAR AND RELATED ANALYTICAL
TECHNIQUES**



XA9950308

Research Contract No. 9482/RB:

**WORKPLACE MONITORING AND OCCUPATIONAL HEALTH STUDIES IN
THE ŠOŠTANJ THERMAL POWER PLANT, SLOVENIA**

Responsible organization: Jožef Stefan Institute, Ljubljana, Slovenia

Chief Scientific Investigator: Radojko Jaćimović, B.Sc.

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WORKPLACE MONITORING AND OCCUPATIONAL HEALTH STUDIES IN THE ŠOŠTANJ THERMAL POWER PLANT, SLOVENIA

R. Jačimović¹, A.B. Kobal², B. Stropnik³, I. Falnoga¹, Z. Jeran¹, A.R. Byrne¹

¹Jožef Stefan Institute, Jamova 39, POB 3000, SI-1001 Ljubljana, Slovenia,

²Idria Mercury Mine, Arkova 43, SI-5280 Idria, Slovenia,

³ERICo, Koroška 58, POB 22, SI-3322 Velenje, Slovenia

Up to now, only a few investigations have been performed in the Šoštanj Thermal Power Plant (TPP) involving comprehensive studies of trace elements, toxic elements, heavy metals and radionuclides in the workplaces. The aim of the project is development and application of nuclear and nuclear-related analytical techniques for workplace pollution and occupational health studies, leading to formation of a database concerning the trace element air pollution inside the Šoštanj Thermal Power Plant. In this report, the emphasis is on the methodology and analytical development (neutron activation analysis, X-ray spectrometry, total-reflection X-ray fluorescence (TXRF) spectroscopy and proton induced X-ray emission (PIXE)), and to a lesser extent on the results obtained up to now. Analytical results for several certified reference materials of similar matrix as the real samples investigated were obtained. Results obtained by the k_0 -standardization method and XRF technique for aerosols (coarse and fine fractions) are also presented and discussed.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

The general scope of the project is a better knowledge of the state of air pollution in the Šoštanj Thermal Power Plant by performing workplace monitoring and occupational health studies involving determination of trace element air pollution from industrial emissions by analysing airborne particulate matter (APM) and biological samples taken from exposed workers.

Energy production from fossil fuel pollutes the workplace, the surrounding environment and also, because of the use of ash and gypsum in civil engineering, the living environment. Underground lignite mining results in high amounts of coal fly ash and radon productions. Use of the ventilating system produces high values of ash and radon in the environment. Coal, after drying on the tips, is transported to the TPP on beltways which cause large amounts of coal dust to be dispersed into the environment.

The Šoštanj Thermal Power Plant with an installed electric power capacity of 745 MW consumed 3,8 million tons of lignite coal in the year 1992. This represents 90% of the total coal mine production, of which it is estimated only 32% is used effectively. The sulphur content of the coal is 1.3%. The SO₂ emission factor in the TPP is 0.85; the emissions in the year 1992 were 94,120

tons of SO₂ (without desulphurization), 6,085 tons of fly ash, 9,009 tons of NO_x and unknown quantities of other pollutants. The SO₂ concentration in the flue gases is 3 to 8 gm⁻³ and of NO_x 0.2 to 0.6 gm⁻³. A schematic diagram of the plant is shown in Fig. 1. Yearly ash production is up to 800,000 tons. The ash disposal site has a surface of 0.5 km². Part of this surface is covered with grass while the rest flooded with water.

In the some yearly periods (late autumn, winter and early spring) the workplaces are contaminated not only by ash and coal dust but also with high concentration of organic pollutants. After coal is burned in the furnace system of the TPP, the elements contained in coal separated into two major fractions; those which are volatile and are transported with flue gases, and those which mainly remain in the ash or furnace slag. The passage of trace metals through the boiler to the stack is mainly dependent on the combustion temperature, the residence time of the ash in the hot combustion zone of the boiler and the efficiency of the electrostatic precipitators. Higher temperatures and longer ash residence times favour the evaporation of volatile trace metal compounds from the ash (coal). Slag tap boilers (combustion temperature around 1973 K, residence time 1-2 h) normally show higher enrichment ratios for smaller particles, which preferentially pass the electrostatic precipitations, than do dry bottom boilers (combustion temperature around 1625 K, residence time 2-5 s). Šoštanj TPP is a dry bottom boiler (BABCOCK). During combustion, through the volatilization and subsequent condensation mechanism during flue gas cooling to 450 K, before exhaust to the atmosphere, some elements are enriched (10 to 40 times) [12] in the finest size fractions.

Workers at the Thermal Power Plant in some sectors are exposed to high levels of coal dust, in others to dusty operations with ash and electrostatically precipitated fly ash, and in addition a force of welders is employed for maintenance and construction tasks. Contact with coal and fly ash lead to wear of milling and transporting devices. To keep these devices in operation they must sometimes be repaired by welding with a special metal alloy which has a high content of heavy metals. Welders work 5 to 6 hours per day (50 m of weld) and they are protected only from UV light. They are exposed to high concentration of metals in the inhaled welding fume. In the particular working conditions sometimes welders are exposed to high concentrations of fume. In some cases other workers are exposed to coal dust; other are exposed to very high concentrations of fly ash. The major pollutants of concern in ash and coal are quartz particles, natural radioactive radionuclides from the ²³⁸U chain (the ash contains 25-30 mg/kg uranium), polycyclic aromatic hydrocarbons, heavy metals and other toxic microelements.

It is the goal of the project that on its successful completion, an improvement in the development and applications of nuclear and nuclear-related analytical techniques will be achieved, and a database concerning trace element air pollution in the TPP will be obtained, possibly leading to appropriate decisions in environmental control. Particular research objectives are:

1. To improve and further develop analytical techniques for multielement characterization of the materials analysed, including speciation of some particular pollutants (e.g. Hg, Cr).
2. To determine the actual exposure of the three critical groups of workers (those exposed to coal dust, those exposed to coal ash and welders).
3. To carry out a programme of health checks on the exposed workers.
4. Following a preliminary evaluation of 2. and 3., to prepare, carry out, and monitor technical solutions for reducing exposure, improving working conditions and evaluating and monitoring the health status of the critical groups.

Close collaboration has been established between the Jožef Stefan Institute, its associated partner ERICo Velenje (**E**cological **R**esearch & **I**ndustrial **C**ooperation), the Institute for Occupational Health, Traffic and Sport, Ljubljana and with the Idria Mercury Mine (now closed). ERICo is giving us assistance in collecting and analysing aerosols, and the Institute for Occupational Health, Traffic and Sport, Ljubljana, is contacted on behalf of the Šoštanj TPP.

2. METHODS

2.1. Sample collection

To perform the planned programme in the Šoštanj TPP, 10 sampling workplace sites were chosen. Five of them were exposed to high concentration of coal dust and five with ash. The sampling sites were chosen at the following workplaces:

- The boiler bunkers, Block 5, exposure - coal
- The internal transport of ash, Block 4, exposure -ash
- The internal transport of ash, Block 5, exposure - ash
- The boiler bunkers, Block 4, exposure - coal
- Control of the coal transportation system PE-24, exposure - coal
- Internal transport of ash, Block 2, exposure - ash
- The boiler bunker, Block 1-3, exposure - coal
- The external transport of ash, Block 1-3, exposure - ash
- Control of the coal transportation system PE-05, exposure - coal
- First repeated reheater unit PP1, Block 5, exposure -ash.

Aerosols are collected by means of an in-house constructed single jet sampler [1], with a cut-off point of $\sim 2.5 \mu\text{m}$. The sample inlets are positioned 1.8 m above the ground. The fraction ~ 2.5 to $10 \mu\text{m}$ is collected on a Nuclepore polycarbonate membrane filter (37 mm diameter, pore size $0.45 \mu\text{m}$), with free air flow reduced to a diameter of 13 mm in order to achieve a higher concentration of coarse particles in the central part of the filter. The particulate fraction finer than $\sim 2.5 \mu\text{m}$ is collected on a Nuclepore

polycarbonate membrane filter (47 mm diameter, pore size 0.45 μm). Both filters are held in the original Nuclepore holders. The air flow rate through the separator and both filters is regulated by a critical orifice between the filters and a GAST oil-less diaphragm vacuum pump (type DOA). The flow rate is not constant and it decreases by up to 50% from the beginning to the end of the sampling period. The arithmetic median value of the flow rate is about 400 L·h⁻¹, representing approximately one third of the rate of human breathing. The flow rate is measured by a rotameter at the beginning of sampling, checked every second day and finally at the end of the sampling period. The effectiveness of the separator in defining the two fractions was controlled by examination of the collected particulates under a scanning electron microscope (LEITZ - AMR); no evidence for collection of particles greater than 2.5 μm in the fine fraction was ever found. Sampling times vary, depending on the minimal flow rate necessary for successful operation of the separator and determination of the content of air particulates, being from 3 to 14 days.

2.2. Sample preparation

The procedure for samples to be analysed by instrumental neutron activation analysis is as follows:

Two-hundred milligram aliquots of SRMs are packed in polyethylene ampoules (Kartell, Noviglio, Italy), together with an Al-0.1% Au alloy wire (Central Bureau for Nuclear Measurements, Geel, Belgium) of 1.0 mm diameter and a 0.125 mm Zr foil (Goodfellow, Cambridge, UK), which serve as comparator and fluence rate monitors.

APM loaded filters are pelletised with a manual press (Mod. 25011, Specac, UK) in a pellet die of 5 mm diameter and packed the same way as SRMs.

The procedure for samples to be analysed by energy dispersive X-ray fluorescence spectrometry is as follows:

Loaded filters are weighed on a Mettler balance AE 163 having a precision of 10 μg (Mettler Instrumente AG, Switzerland), after neutralising the charge with a Nuclepore static eliminator (Nuclepore, Cambridge, USA). Filters are kept in Petri dishes prior to analysis.

2.3. k_0 -based instrumental neutron activation analysis (INAA)

All irradiations are made in the channels of the TRIGA Mark II reactor of the Jožef Stefan Institute (IJS): for short irradiation (from 2 to 5 min) in the pneumatic tube at a thermal flux of $3.5 \cdot 10^{12}$ neutrons·cm⁻²·s⁻¹, and for longer irradiations in the carousel facility at a thermal neutron flux of $1.1 \cdot 10^{12}$ neutrons·cm⁻²·s⁻¹ (irradiation time for each sample was 18-20 h). After irradiation the samples are transferred to clean 5 ml polypropylene mini scintillation vials (Atom Medical Ltd., Hove, UK) for measurement. The radionuclides used in the determination of up to 50 elements in each sample,

their half-lives and gamma-energies measured are given elsewhere [2]. The samples are measured on two HP Ge detectors (Ortec, USA) with 17 and 20% relative efficiencies [18] which are connected to a Canberra Series 90 multichannel analyser (Canberra Packard, USA), and a new detector (also manufactured by Ortec) with 40% relative efficiency connected to a Canberra S 100 multichannel analyser. For the k_0 standardization method we need absolutely calibrated detectors [18]. For short half-life nuclides samples are measured 90 seconds and 2.5 hours, and for medium and long-lived nuclides 2 days, 8 days and 15 days after the end of irradiation. Measurements are performed at such a distance that the dead time is kept below 10% and random coincidences are negligible. The Au comparators are measured at a large distance (i. e. 16 - 20 cm) and their geometry is approximated by a small cylinder. The Zr foil is measured in the form of discs, and, again, the dead time is kept below 10%. Spectra are processed by the SAMPO 90 program [3]. Effective solid angle calculations are made using the SOLANG program [4]. Elemental concentrations are calculated by the ROMOS program [5]. The relevant nuclear constants (i. e. k_0 , Q_0 factors, etc.) are taken from the literature [6-9]. At this moment we have installed a new software packet KAYZERO[®]/SOLCOI[®] which includes the above two steps [17].

2.4. Energy dispersive X-ray fluorescence spectrometry (EDXRF)

Samples are placed on an in-house constructed automatic sample changer carousel facility with a capacity of 10 specimens. Two different set-ups are used for EDXRF analysis: (i) a 1 GBq ^{109}Cd excitation source (Isotope Products Laboratories, Burbank, USA) and a Si(Li) detector (Canberra Industries, Meriden, USA) with an active area of 30 mm², thickness of 3 mm and FWHM of 165 eV at 5.9 keV coupled to a Canberra S 100 multichannel analyser (MCA); (ii) a 1 GBq ^{241}Am excitation source or a 1.8 GBq ^{55}Fe source (both supplied from Isotope Products Laboratories) and a low energy Ge detector (Canberra Industries) with an active area of 30 mm², thickness of 5 mm and FWHM of 140 eV at 5.9 keV. Spectra are processed and quantitative analysis performed using AXIL-PC and QAES (Quantitative Analysis of Environmental Samples) software (Canberra Industries). Both systems were calibrated using NIST SRM 1832 XRF Thin Film Standards for Al, Si, Ca, V, Mn, Co, and Cu, and NIST SRM 1833 XRF Thin Film Standards for Si, K, Ti, Fe, Zn, and Pb.

2.5. Total-reflection X-ray fluorescence (TXRF)

Total reflection XRF spectroscopy is an analytical technique which is characterised by a few orders of magnitude better sensitivity than conventional X-ray fluorescence spectroscopy. The technique is based on the total reflection of the incident excitation beam from the sample substrate which is usually an optically polished quartz plate. The excitation beam must be well collimated in order to be able to adjust for as possible part of the beam the incident angle of few *mrad*, what is usually the value of the critical angle for X-rays of energy around 20 keV.

The TXRF system is assembled using an X-ray spectrometer, a tube excitation system and the total reflection module. The X-ray spectrometer is based on a Si(Li) detector (EG & G Ortec, 30 mm² x 3 mm sensitive volume, 25 µm Be window), with a resolution of about 170 eV at 5.9 keV. The electronics system (Canberra), consists of a fast spectroscopy amplifier M 2024, M 8075 ADC, an M 3105 power supply and an S-100 PC based MCA. This system contains pile up rejection (PUR) circuitry, which has proved indispensable for data acquisition involving the high counting rates needed when the dead time exceeds 10% [20].

The TXRF technique has proved to very successful in the environmental analysis of rain water, river water and sea water, but it can also be applied in atmospheric chemistry for aerosol analysis [21].

2.6. Particle induced X-ray emission (PIXE)

In atmospheric pollution studies, ion beam analysis using accelerators has found a number of successful applications since the early 1970s. Among them, particle induced X-ray emission (PIXE) has gradually developed into a standard tool in this field; the application of PIXE to atmospheric research makes use of all its advantageous features. Routine PIXE analysis can be performed with quite a simple electrostatic accelerator that requires only a minimum of technical assistance. The high X-ray production cross-sections for elements with Z values between 10 to 90, and at the same time low contributions to the X-ray spectral background, mainly due to the bemsstrahlung of secondary electrons in the sample matrix, make PIXE a very sensitive analytical tool compared with other nuclear and atomic spectrometric techniques; relative detection limits, for the majority of elements above Al, are of the order of 10⁻⁵ - 10⁻⁷. The best overall performance is attained by using light ions, especially 2-3 MeV protons.

The experimental conditions of the PIXE measurements were as follows: a proton beam energy of 1.39 MeV and a proton current of ≈ 10 nA that was diffused by a gold foil to make it more homogeneous. The proton dose on each target was preset at 5 µC. The beam spot was 5 mm x 5 mm. The X-ray detector was an intrinsic HPGe detector with an 8 mm Be window. The detector had an area of only 25 mm² and the resolution achieved was 145 eV at 5.9 keV. Spectrum analysis was performed by the AXIL program [22] and quantitative analysis was based on a computer program developed in the laboratory. The calibration for quantitative analysis utilised measurements on a thin sample prepared by applying a known amount of a multielement standard solution, containing a set of elements (K, Ca, Cr, Fe, Ni, Zn, As, Br, Rb, Sr and Pb) to a Mylar foil on an area smaller than the proton beam. The absolute load of elements did not exceed 0.3 mg.

3. RESULTS AND DISCUSSION

The concentrations of dust in air was several higher at the workplaces than in the unloaded environment. In enclosed places below the electrostatic filters the concentrations were extremely high but not higher than the values suggested by WHO as limit values. In the boiler, after the heating process was stopped, concentrations of aerosols in air were extremely high and exceeded the permissible values. Beside that, some elements have an affinity for the respirable fraction of dust, leading to high occupational exposure at the workplace from heavy metals in respirable particles, which have a dominant effect on the workers' health.

Concentrations of elements in the respirable fraction of aerosols, coming from coal fly ash and coal dust at selected workplaces, are shown in Table 1 and Table 2, respectively. All results were obtained using the XRF technique. A comparison between these workplace areas in the Šoštanj TPP and an urban area near Šoštanj is presented in these Tables, as well as the limiting concentrations for workplaces defined by local law [23] and WHO [24].

In 1994, much effort was put into quality assurance. Thus, as well as the analysis of IAEA Lichen research material and the APM collected on filter media (prepared by S. Landsberger), some other standards (SRMs) or certified reference materials (CRMs) were analysed by the proposed methods/procedures. The analytical results for several NIST SRMs, namely SRM No. 1633a Coal Fly Ash, SRM No. 1570 Spinach, SRM No. 3087 Metals on Filter Media, and for BCR CRM No. 128 Fly Ash on Artificial Filter are presented in [15]. The results for NIST SRM No. 1643c Trace Elements in Water are presented in Ref. [16].

The results are reported as arithmetic means of several independent determinations with uncertainty values as 95 % confidence intervals, combined in quadrature with an additional 3.5% estimated systematic error as reported by De Corte [10] for the overall average uncertainty for k_0 - standardization NAA. In these two tables certified values and "consensus" values as defined by Gladney et al. [11] for the elements determined are also given.

Table 1. Concentration of elements in the respirable fraction of aerosols coming from coal fly ash ($\mu\text{g m}^{-3}$) [19].

	Sampling sites			PE-24	PE-05	Block 1-3	Block 4	Block 5
	Limiting concentrations			Coal control	Coal control	Bunkers	Bunkers	Bunkers
	Workplace	Urban area		1992-05-21	1992-06-02	1992-05-29	1992-05-18	1992-04-29
		WHO	Average Škale					
Mass	10000	50	31	1220	2290	5090	860	960
Al			0.246	29	50.2	26.7	36.8	38.6
Si			0.333	72.7	119	60.1	94.7	97.4
S			1.814	15.2	16.7	12.3	15.1	14.1
Cl	2000		0.024	2.77	8.94	2.06		0.69
K			0.141	6.93	11.1	6.02	9.04	7.02
Ca	5000		0.157	29.5	36.3	18.2	29	17.4
Ti	10000		0.011	1.44	2.27	1.03	1.71	1.6
V	100	1	0.003		0.13	0.36		
Cr	1000	1	0.003				0.32	
Mn		1	0.015	0.37	0.86	0.22		1.29
Fe	10000		0.164	28.3	46.2	16.9	30.9	24
Co	100				0.25			1.19
Ni	500	1	0.006					0.42
Cu	1000		0.004			0.03	0.15	0.12
Zn	5000		0.038	0.66	0.61	0.35	0.48	0.27
Pb	150	0.5	0.045	0.39	0.49	0.12	0.45	
Rb				0.15	0.13	0.07	0.19	0.36
Sr			0.006	0.19	0.31	0.1	0.18	0.26
Y	1000				0.04			2.24
Zr	5000		0.004	0.09	0.87	0.03		
Nb				0.08				
Mo	5000			0.07	0.04		0.08	
Ga								
Br	700		0.007					
U	50							

Table 2. Concentration of elements in the respirable fraction of aerosols coming from coal dust ($\mu\text{g m}^{-3}$) [19].

	Sampling sites			Block 2	Block 1,2,3	Block 4	Block 5	Block 5
	Limiting concentrations			Internal transport	Pumping station	Internal transport	Internal transport	PP1 reheater
	Workplace	Urban area		1992-05-29	1992-06-02	1992-05-07	1992-05-12	1992-10-30
		WHO	Average škale					
Mass	10000	50	31	7	96	450	310	34500
				70	68	4880	3290	304000
Al			0.246		0.006	12.2	10.3	2370
Si			0.333	0.2	0.56	29.7	31.3	6230
S			1.814	1.91	2.86	6.3	6.75	1070
Cl	2000		0.024	0.46				
K			0.141		0.3	3.42	3.92	1080
Ca	5000		0.157	0.26	2.49	13.5	16.9	1420
Ti	10000		0.011	0.009	0.03	0.7	0.64	145
V	100	1	0.003	0.005		0.01	0.008	5.16
Cr	1000	1	0.003					4.1
Mn		1	0.015					45.5
Fe	10000		0.164	0.26	0.48			5620
Co	100							28.3
Ni	500	1	0.006		0.01			3.72
Cu	1000		0.004					5.25
Zn	5000		0.038	0.02	0.05			113
Pb	150	0.5	0.045	0.05	0.07			29.1
Rb					0.02			16.5
Sr			0.006					27.7
Y	1000				0.03			27.7
Zr	5000		0.004					11.3
Nb								1.83
Mo	5000							6.52
Ga								4.52
Br	700		0.007					0.18
U	50							1.92

Concerning the quality control of the results by k_0 -INAA, or NIST SRM 1633a Coal Fly Ash, 32 elements were quantitatively determined. The concentrations obtained for 12 out of 13 of the elements were statistically indistinguishable from the certified values. For the remaining 19 elements, for which no certified values exist, 18 experimentally obtained values were statistically indistinguishable from the "consensus" values. For Br, only 1 value was found in the literature, so no reliable comparison could be made.

Since the ED XRF technique requires demanding preparation of the target and a knowledge of the attenuation of excitation and fluorescence rays in the sample when thick targets are applied, this analytical tool was used only for thin (i. e. filter) samples.

The results obtained are presented in Ref. [15]. Since the values quoted in the certificate of analysis for the NIST SRM 3087 Metals on Filter Media (see Table 4 in Ref. [15]) are in $\mu\text{g}/\text{filter}$, the same unit is used for the results of our analyses. Uncertainties are expressed as two standard deviations, in order to be comparable with the certificate, where they are also quoted in the same way. In addition, the certified values are also expressed in $\mu\text{g}\cdot\text{cm}^{-2}$, to be comparable with the results for the other CRMs. It is evident from Table 4 (Ref. [15]) that for all 9 elements certified no statistical difference between the certified and experimentally obtained values could be found, with the exception of Mg, which was below the detection limit (a vacuum should be applied to the system in order to determine this element).

A summary of the analytical results by ED XRF for BCR CRM No. 128 Fly Ash On Artificial Filter is given in Ref. [15]. It can be seen that for 5 elements out of the 10 certified and for one among the 4 elements which are not certified, quantitative data were obtained. Unfortunately, only the data for Fe and Zn can be accepted as analytically reliable, with uncertainties of 5.5 % and 10 %, respectively. For the other 4 elements Cu, Mn, Ni and Pb, the experimentally obtained uncertainties are unacceptable, ranging from 44 % for Pb to 77 % for Ni. When comparing elemental values in surface density units, $\mu\text{g}\cdot\text{cm}^{-2}$, for NIST SRM 3087 and BCR CRM No. 128, it could be noticed that the loadings for the first SRM are approximately two orders of magnitude higher than for the latter one. For the elements As, Cd, Co, Cr, Hg, Th and V in BCR CRM No.128, the mass fractions on the loaded filter are below the detection limit of the method applied, and it can be concluded that a loading of roughly $0.1 \mu\text{g}\cdot\text{cm}^{-2}$ per element is required for quantitative analysis using our ED XRF system.

Using the k_0 -standardization method of NAA as implemented in this study, 50 elements can in principle be determined from a single irradiation. In real samples, quantitative data for approximately 30 elements could realistically be expected, with the elemental values statistically indistinguishable from certified ones (20 out of 21 as presented in Ref. [15]). Using an additional short irradiation (i.e. 5 min), data for an additional 12 elements could be obtained (Al, Cl, Cu, Dy, I, Mg, Mn, Ni, Si, Ti, V, Y). It is well known that Pb cannot be determined by NAA at $\mu\text{g}\cdot\text{g}^{-1}$ level, and some other

technique (including ED XRF) should be applied for analysis of this heavy metal.

Using ED XRF with the set-up described, up to 20 elements having $Z \geq 13$ were usually sought: (i) Si, P, S, K, Ca, Ti and V using an ^{55}Fe exciting source connected to a low energy HP Ge detector, (ii) Cr, Mn, Fe, Ni, Cu, Zn, Pb, Br, Sr and Zn using a ^{109}Cd exciting source connected to a Si(Li) detector, and (iii) Cd, Sb and Ba using a ^{241}Am exciting source connected to a low energy HP Ge detector. This method is much faster than INAA, requiring less than two hours per measurement, thus allowing a throughput of about 60 samples per week when using a sample changer and two detectors. It is suitable for processing a large number of samples of similar matrix composition such as APM collected on filters; however, the quantity of air sampled should be such as to allow elemental surface densities of approximately $0.1 \mu\text{g}\cdot\text{cm}^{-2}$ in order to ensure acceptable quantitative analysis.

Both techniques are currently being implemented for the analysis of biological samples, lichens as biomonitors for air pollution, and for the analysis of APM collected by an in-house constructed single-jet APM separator [1], in the framework of the air pollution survey on the workplaces. On the basis of experience obtained in implementing both methods, ED XRF was chosen for the analysis of APM, and the INAA procedure as a control method for APM, as well as for the analysis of bulk precipitation and lichens. The APM separator used is working at an average flow-rate of $0.4 \text{ m}^3\cdot\text{h}^{-1}$ for up to 14 days, collecting up to 1 mg APM cm^{-2} , which allows quantitative determination of 15 elements, on average, including Si, S, Ni, Cu and Pb, thus representing elements complementary to the INAA data. Some preliminary results concerning air pollution obtained by measuring trace elements in APM and bulk precipitation have already been published, and the details can be found elsewhere [12-14].

4. PLANS FOR FUTURE WORK

It is planned to continue systematic trace element air pollution monitoring and research in the workplaces of the Šoštanj thermal power plant using nuclear and nuclear-related analytical techniques. Airborne particulate matter and biological samples taken from occupationally exposed humans will be systematically analysed.

The group of workers who are exposed to dust is relatively small. For such studies and for comparison with previous results on the negative health effect on workers we need to extend the number of persons in the group. If we, as a group in the IAEA project have the same or similar programme as the groups from other countries involved in the coordinated project we could have a larger sample and also be able better to predict health effects on persons in the workplace.

Thus the aim of our programme is:

1. Sampling two dust fractions, separated by aerodynamic diameter into a fine fraction (0-2.5 μ m) and a coarse fraction (2.5-10 μ m),
2. Use of a Casella personal sampler with centrifugal separator facility and also other sampling devices for comparison.
3. To determine the mass fractions of dust based on the gravimetric method.
4. To determine elemental concentrations with various methods (EDXRF, TXRF, PIXE, k_0 -INAA).
5. To determine concentrations and speciation of highly toxic elements in the dust (Cr³⁺ and Cr⁶⁺).
6. To determine concentrations of organic pollutants using different methods of sampling and analytical techniques.
7. To determine element concentrations in appropriate human biological samples based on medical advice.

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Title of Project:

**WORKPLACE MONITORING AND RELATED
HEALTH HAZARD EVALUATION IN SOUTH
AFRICAN MINING AND MINERAL PROCESSING
INDUSTRIES BY APPLICATION OF NUCLEAR
AND RELATED ANALYTICAL TECHNIQUES**

Institute:

Atomic Energy Corporation of
South Africa Limited
P.O. Box 582
Pretoria 0001
South Africa

Chief Scientific Investigator: Arnaud Faanhof

Project Commencement Date: 15 December 1996

The Impact of Natural Radioactivity in the Mining and Mineral Processing Industries

A Case Study on Some Industries

Contribution to the first Research Co-ordinating Meeting on "Assessment of levels and health-effects of airborne particulate matter in mining, and metal refining and working industries using nuclear and related analytical techniques", Vienna, IAEA Headquarters, 20 - 24 October 1997.

Dr Arnaud Faanhof
Consulting Scientist
PO Box 582
Pretoria, 0001
South Africa

1. OBJECTIVE

To present the results of various observations of the assessment of natural radioactivity in a limited suite of mining and mineral processing industries in Southern Africa, and to illustrate the potential of INAA in the additional assessment of trace elements.

2. SCOPE

The information is based on a compilation of numerous data as analysed by the Radioanalytical Laboratories of the AEC. The information provided is meant to be only illustrative to possible problems with natural radioactivity in the mining and mineral processing industries.

3. INFORMATION ON THE SURVEY

3.1 Background information

Data were chosen randomly from a vast data base of information. The nuclear and related analytical techniques applied were mainly based on instrumental neutron activation analysis and gamma-ray and alpha-particle spectrometry. The main objective has been to focus on natural radioactive nuclides, while the potential of INAA for elemental analysis of respirable airborne dust is being illustrated. The radiological impact has been assessed according to dose conversion factors provided in the IAEA Safety Series 115, 1996.

3.2 Sampling procedures

The South African Department of Mineral and Energy Affairs has published guidelines for the gravimetric sampling of airborne particulates for risk assessment in terms of the occupational diseases in mines and works act no 78 of 1973. These guidelines are updated regularly (latest version: third edition, February 1994, Reference GME 16/2/3/2/3).

This document provides extensive information on amongst others the sampling strategy, sampling instruments, standard procedures for the assembly of the sampling train and formulae to calculate TWA-CONC (Time-Weighted Average Concentration) and AQI (Air Quality Index). Furthermore, TLV's (Threshold Limit Values) for airborne pollutants are specified by the GME (Government Mining Engineer) from time to time, and approved accredited authorities for sampling and analyses are provided.

4 ANALYTICAL

4.1 Scope of the contribution

The main interest for Radioanalytical Laboratories in this project is in the analysis of the nuclides of the natural thorium, actinium and uranium series because these elements: (i) play a crucial role in the study of radioactivity in the environment which is one of its core competencies, and (ii) are determined routinely for various clients in the mining and mineral processing industries in Southern Africa.

Instrumental neutron activation analysis (INAA) is the preferred technique for the determination of trace quantities of a variety of elements including uranium and thorium, while radioanalytical techniques are applied to quantify other nuclides of the natural decay series.

4.2 Methods used by Radioanalysis

Uranium is determined by delayed neutron counting using a 20/15/45 second measurement cycle (*ie* neutron irradiation/decay/count intervals) on the automatic RINGAS system (Routine Instrumental Neutron and Gamma Analysis System). Corrections were made for the contribution from Th fission. All the other elements were determined by conventional neutron irradiation, followed by γ -spectrometric analysis of the activity induced in the material. In order to measure as many elements as possible, different irradiation facilities of the Safari-1 reactor and irradiation/decay/measurement cycles were used:

- for short-lived nuclides: 7s/30s/120s, using the Cd-lined irradiation position of RINGAS (epithermal neutrons only, Co cadmium ratio about 30, epithermal neutron flux $\sim 3 \cdot 10^{12}$ n.cm⁻².s⁻¹), and a HPGe γ -detector.
- for intermediate nuclides: 35s/3h/10m, using the non-Cd position of RINGAS (thermal neutron flux $\sim 9 \cdot 10^{13}$ n.cm⁻².s⁻¹), followed by another 15m count on the same samples after a 30h decay period respectively.
- for long-lived nuclides: 1h/7d/30m, using the Pneumatic Rabbit System (PRS: thermal neutron flux $\sim 3 \cdot 10^{13}$ n.cm⁻².s⁻¹) for irradiation and a HPGe well-type γ -detector for counting. Corrections for variation in the neutron flux were made using 25 mg Fe flux monitor rings with each sample, and the ⁵⁹Fe activity measured by γ -spectrometry (5m counting; HPGe well-type detector).

In some cases data for the same element are obtained from two measurement cycles. Typical data are provided for the applied irradiation/decay/counting schedules. It should be emphasized that relative data are provided to illustrate the technique rather than to provide absolute data for hazard assessment.

Radionuclide measurements were performed by α -particle spectrometry (72 hours) directly on the respirable dust collected on the filters. Final data are calculated for the long-lived α -active nuclides by evaluation of the α -spectra in combination with the uranium and thorium data obtained from INAA on the same sample.

Typical irradiations and measurements are carried out on the respirable airborne dust collected during an 8 hour shift. Personal cyclone type samplers are used which are attached close to the chest of workers. The uranium and thorium activities in the samples are calculated from the corresponding concentration values. Reference standards are prepared by weighing suitable volumes of standard solutions (eg Merck Titrisol and standard solutions for atomic absorption spectrometry), evaporating the liquid and sealing the container ultrasonically. High purity polyethylene containers are used for INAA (hxd ~ 1x1 cm).

The following international Certified Reference Materials are normally analysed together with the samples studied in INAA:

- IAEA SD-M-2/TM (Trace elements in lake sediment homogenate)
- IAEA Soil-7 (Major and trace elements in soil sample)
- IAEA MA-A-2/TM (Trace elements in fish flesh homogenate)
- SABS SARM-19 (Major and trace elements in OFS Coal)

4.3 Results

Various data obtained for respirable airborne dust will be presented at the meeting. One example is presented in the Annexure 1.

4.4 Evaluation

A compilation of the observations is:

INAA

This is a well established technique to determine a wide variety of elements in samples with low absolute quantities of the matrices of interest; as e.g. collected respirable airborne dust. Alternatives are PIXE and ICP-MS (on dissolved samples).

Radionuclides

Determination of long-lived α -active nuclides by α -particle spectrometry directly on the collected respirable dust in combination with INAA for uranium and thorium seems to be the only reasonable alternative to assess the radiological impact of respirable dust.

Radiological hazard assessment

Dose conversion factors vary for the individual nuclides of the natural uranium, thorium and actinium decay series. Full nuclide specific analyses are required to assess the full impact of respiration of dust contaminated with radioactivity.

Annexure 1a Inhalation of dust (slow uptake): Exposure to workers in a Heavy Mineral Industry

	Sv/Bq	Sv/Bq	Measured absolute activity in mBq						
	1 μ m	5 μ m							
			Mo-3	Mo-15	Mo-18	Mo-20	Zr-1	Zr-5	Zr-8
U-238	7.30E-06	5.70E-06	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Th-234*	7.30E-09	5.80E-09	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Pa-234m	NA	NA	10.21	2.78	4.85	4.13	0.29	0.31	0.34
U-234	8.50E-06	6.80E-06	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Th-230*	1.30E-05	7.20E-06	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Ra-226*	3.20E-06	2.20E-06	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Rn-222	NA	NA	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Po-218	NA	NA	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Pb-214	2.90E-09	4.80E-09	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Bi-214	1.40E-08	2.10E-08	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Po-214	NA	NA	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Bi-210	8.40E-08	6.00E-08	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Pb-210	8.90E-07	1.10E-06	10.21	2.78	4.85	4.13	0.29	0.31	0.34
Po-210	3.00E-06	2.20E-06	10.21	2.78	4.85	4.13	0.29	0.31	0.34
U-235	7.70E-06	6.10E-06	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Th-231*	2.90E-10	3.70E-10	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Pa-231*	3.20E-05	1.70E-05	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Ac-227	6.60E-05	4.70E-05	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Th-227*	9.60E-06	7.60E-06	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Ra-223*	6.90E-06	5.70E-06	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Rn-219	NA	NA	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Po-215	NA	NA	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Pb-211	3.90E-09	5.60E-09	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Bi-211	NA	NA	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Tl-207	NA	NA	0.49	0.13	0.23	0.20	0.01	0.01	0.02
Th-232*	2.30E-05	1.20E-05	40.12	11.32	18.85	17.28	0.34	0.68	1.64
Ra-228*	2.60E-06	1.70E-06	40.12	11.32	18.85	17.28	0.34	0.68	1.64
Ac-228	1.40E-08	1.20E-08	40.12	11.32	18.85	17.28	0.34	0.68	1.64
Th-228*	3.90E-05	3.20E-05	40.12	11.32	18.85	17.28	0.34	0.68	1.64
Ra-224*	2.90E-06	2.40E-06	40.12	11.32	18.85	17.28	0.34	0.68	1.64
Rn-220	NA	NA	40.12	11.32	18.85	17.28	0.34	0.68	1.64
Po-216	NA	NA	40.12	11.32	18.85	17.28	0.34	0.68	1.64
Pb-212	1.90E-08	3.30E-08	40.12	11.32	18.85	17.28	0.34	0.68	1.64
Bi-212	3.00E-08	3.90E-08	40.12	11.32	18.85	17.28	0.34	0.68	1.64
Po-212	NA	NA							
Tl-208	NA	NA							

Continued

		m3	0.23	0.23	0.22	0.23	0.23	0.23	0.23
	Sv/Bq	Sv/Bq	Calculated dose in uSv/a						
	1 u m	5 u m							
U-238	7.30E-06	5.70E-06	746.64	201.63	365.46	304.56	21.15	22.58	24.55
Th-234*	7.30E-09	5.80E-09	0.75	0.20	0.37	0.30	0.02	0.02	0.02
Pa-234m	NA	NA							
U-234	8.50E-06	6.80E-06	869.37	234.77	425.53	354.62	24.63	26.29	28.59
Th-230*	1.30E-05	7.20E-06	1329.63	359.06	650.82	542.36	37.66	40.22	43.73
Ra-226*	3.20E-06	2.20E-06	327.29	88.38	160.20	133.50	9.27	9.90	10.76
Rn-222	NA	NA							
Po-218	NA	NA							
Pb-214	2.90E-09	4.80E-09	0.30	0.08	0.15	0.12	0.01	0.01	0.01
Bi-214	1.40E-08	2.10E-08	1.43	0.39	0.70	0.58	0.04	0.04	0.05
Po-214	NA	NA							
Bi-210	8.40E-08	6.00E-08	8.59	2.32	4.21	3.50	0.24	0.26	0.28
Pb-210	8.90E-07	1.10E-06	91.03	24.58	44.56	37.13	2.58	2.75	2.99
Po-210	3.00E-06	2.20E-06	306.84	82.86	150.19	125.16	8.69	9.28	10.09
U-235	7.70E-06	6.10E-06	37.50	10.13	18.36	15.30	1.06	1.13	1.23
Th-231*	2.90E-10	3.70E-10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pa-231*	3.20E-05	1.70E-05	155.85	42.09	76.29	63.57	4.41	4.71	5.13
Ac-227	6.60E-05	4.70E-05	321.45	86.81	157.34	131.12	9.11	9.72	10.57
Th-227*	9.60E-06	7.60E-06	46.76	12.63	22.89	19.07	1.32	1.41	1.54
Ra-223*	6.90E-06	5.70E-06	33.61	9.08	16.45	13.71	0.95	1.02	1.11
Rn-219	NA	NA							
Po-215	NA	NA							
Pb-211	3.90E-09	5.60E-09	0.02	0.01	0.01	0.01	0.00	0.00	0.00
Bi-211	NA	NA							
Tl-207	NA	NA							
Th-232*	2.30E-05	1.20E-05	9244.44	2584.93	4478.83	4017.15	77.92	156.04	374.11
Ra-228*	2.60E-06	1.70E-06	1045.02	292.21	506.30	454.11	8.81	17.64	42.29
Ac-228	1.40E-08	1.20E-08	5.63	1.57	2.73	2.45	0.05	0.09	0.23
Th-228*	3.90E-05	3.20E-05	15675.36	4383.14	7594.54	6811.70	132.13	264.58	634.36
Ra-224*	2.90E-06	2.40E-06	1165.60	325.93	564.72	506.51	9.83	19.67	47.17
Rn-220	NA	NA							
Po-216	NA	NA							
Pb-212	1.90E-08	3.30E-08	7.64	2.14	3.70	3.32	0.06	0.13	0.31
Bi-212	3.00E-08	3.90E-08	12.06	3.37	5.84	5.24	0.10	0.20	0.49
Po-212	NA	NA							
Tl-208	NA	NA							
Total mSv/a			31.4	8.7	15.3	13.5	0.4	0.6	1.2

*= Moderate absorption from the lung