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APPLICATION, MANUFACTURING AND TRENDS IN DEVELOPMENT OF NUCLEONIC GAUGES IN POLAND

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Application, manufacturing and trends in development of nucleonic gauges in Poland

The current status of manufacturing and application of radioisotope gauges in Poland is presented. Metrological performance of the gauges is briefly described and their expected future prospects on the market of the industrial measuring instruments are discussed. Progress in electronic engineering and common use of the microprocessor systems in the radioisotope gauges made it possible the application of sophisticated methods of signal processing and data treatment, as for example statistical multivariate analysis. Some examples of the multivariate calibration of nucleonic gauges are presented. Application of the partial least square regression (PLS) and artificial neural network (ANN) for the calibration of gauges has been shown.

Zastosowania, produkcja i kierunki rozwoju radioizotopowej aparatury przemysłowej w Polsce

Opisano istniejący stan w obszarze zastosowań i produkcji radioizotopowej aparatury przemysłowej. Przedstawiono ważniejsze parametry metrologiczne tej aparatury oraz przedyskutowano jej rolę i miejsce na rynku przemysłowej aparatury pomiarowej. Postęp w elektronice i powszechne stosowanie układów mikroprocesorowych w urządzeniach radioizotopowych stworzyło możliwości wykorzystania złożonych systemów przetwarzania sygnałów i obróbki danych, takich jak np. statystyczna analiza wielowymiarowa. Przedstawiono kilka przykładów zastosowania wielowymiarowych modeli kalibracji w radioizotopowej aparaturze przemysłowej. Pokazano korzyści płynące z zastosowań metody częściowej sumy najmniejszych kwadratów (PLS) i sztucznych sieci neutronowych (ANN) w kalibracji tej aparatury.

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1. INTRODUCTION

The first application of nuclear techniques, including nucleonic gauges in Poland were reported nearly 45 years ago, and in 1961, about 200 radioisotope gauges were already installed in the Polish industry [1]. During the next thirty years, manufacturing, installation and servicing facilities have been built enabling the application of nucleonic gauges in the industry on a relatively large scale. Since the beginning of the 90's decade, profound reconstruction of the Polish economy has started. The introduction of market economy rules caused, sometimes temporary, reduction of the demand from the industry on the measuring and automatic control devices. Such a situation influenced the manufacturers of that instrumentation and their production capacity had to be considerably reduced. Moreover, the competition of foreign firms offering their products to the industry had also some impact on the position of domestic manufacturers of radioisotope gauges.

All those factors determined the scope of the market for the radioisotope gauges in Poland. According to data of the National Atomic Energy Agency (NAEA), the following numbers of licenses for using radioisotope and radiation sources were issued till the end of 1997 [2]:

Medical sources and accelerators	110
Industrial and geological field research	200
Radioisotope gauges	1280
Firms installing gauges and smoke detectors	410
Industrial and research laboratories (open sources)	260
Industrial and research laboratories (sealed sources)	280
Production, transport and sales of radioactive materials	110

Total, more than 2800 enterprises have obtained licenses for using radioactive sources. Only in 1997, the NAEA has issued about 600 licenses (including annexes to the existing ones) for activities connected with radiation sources. Medical and industrial instrumental X-ray sources are not included in the above data.

The number of the issued licenses for the usage of gauges containing a radioisotope source is not always the same as the number of installed or operating devices in the industry. However, they show an image of the scale of the production and application of the nucleonic gauges in Poland. Practically there are three main manufacturers of those instruments: the Polon-ZOT Ltd., the Institute of Nuclear Chemistry and Technology (INCT) and the Center for Electrical Engineering and Automation in Mining (EMAG) where the gauges for coal mines were developed and are being produced. There are also a few firms providing the installation and service facilities.

Beside manufacturing, some research are being conducted directed towards the development of new gauges as well as the introduction of new technologies into the designed gauges to expand their scope of applications. They resulted, for example, in the development of a system for continuous ash content measurement based on natural radioactivity or design radioisotope instruments where multivariate calibration procedures have been applied.

The aim of this presentation is to portray the present status of the manufacturing and installation of the radioisotope gauges in Poland and to point out to benefits which can be gained when a multivariate approach is used in the calibration of some types of radiometric instruments.

2. PRODUCTION AND APPLICATION OF RADIOISOTOPE GAUGES IN POLAND

At the end of 1997 more than 1200 radioisotope gauges were operating in the Polish industry. Generally, they are used for the measurement and/or automatic control of such quantities as level, density, thickness, coating thickness, massflow, ash content, acid concentration and airbome dust. There are some specific branches of industry where "traditionally" nucleonic gauges are readily installed, such as sugar-factories (density), sulphuric acid production lines (concentration gauges) or coal mines (ash). A short specification of the nucleonic gauges already installed and operating in the industry is presented in Table 1.

2.1. Level gauges

The majority of level gauges installations are single point measurements based on the gamma-relay type UPR, which has been produced in Poland for more than 20 years. More than 650 gamma relays were installed in Poland and about 430 abroad. Continuous on-line level gauges are based on the application of 2 m long ionization chambers.

The prospect of future application of the single point level gauges seems to be quite good, because up to now there are no alternative method capable to perform contactless measurements of the level in such vessels as storage tanks, hot product bunkers etc.

Table 1. Some nucleonic gauges manufactured in Poland and approximate number of their installations (1998)

Measured quantity	Range and accuracy	Principle of operation. Source and detector	Manufacturer. Units installed
LEVEL			
single point	-	γ-absorption, Cs-137, Co-60 G-M counter	POLON 650
on-line	1-6 m	γ-absorption, Co-60 ionization chamber	2
DENSITY	0.6-3.5g/cm^3 ± 0.3%	γ-absorption, Am-241, Cs-137 ionization chamber	POLON-ZOT 325
THICKNESS			
steel sheets	0.1-4 mm ± 1μm 0.8-8 mm ± 5 μm	γ-absorption, Am-241, Sr-90 ionization chamber	POLON-ZOT 38
foils (Al, plastic)	20-100 μm ± 0.5μm 100-800 μm ± 1μm	β-absorption, Kr-85, Pm-147 ionization chamber	11
basic weights	250-950 g/m^2 ± 1%	β-absorption, Sr-90 ionization chamber	3
pipe walls	2-20 mm ± 1% 10-50 mm ± 1%	γ-absorption, Am-241 ionization chamber	12
COATING THICKNESS			
laboratory	0.2-2 μm ± 5% Au/Cu (example)	β-backscattering Pm-147, Tl-204, G-M counter	INCT 60
on line	Zn/Fe	XRF, Am-241 proportional counter	POLON-ZOT 2
MASSFLOW	belt width-up to 1 m accuracy < ± 1%	γ-absorption, Am-241, Cs-137 ionization chamber	POLON-ZOT 230
SULPHURIC ACID CONCENTRATION	90-99% ± 0.2% H_2SO_4	n-scattering, Pu/Be, He-3 proportional counter	INCT 45
ASH IN COAL			
on-line	3-50% ± 1% ash 2-20% ± 1% moist.	γ-scattering, Am-241 microwaves	EMAG 30
on-line	± 1.5% ash	γ-absorption, scintillation counter, Am-241, Cs-137	3
laboratory	± 1% ash	XRF, Pu-238 proportional counter	
AIRBORNE DUST	5-5000 μg/m^3 ± 2% 2 μg/m^3	β-absorption Pm-147, G-M counter	INCT 20
COMPOSITION	-	XRF, Fe-55, Cd-109, Am-241 proportional counter	POLON/INCT 20

2.2. Density gauges

Radioisotope density gauges maintain their predominant position, compared with instruments operating on other principles. Their main advantage is a contactless measurement in the toughest process environment including hazardous areas. About 50% of the radioisotope density gauges are installed in sugar producing plants where they are used mainly for the automatic control of the production process. The gauges produced by the Polon-ZOT can measure density within the range 0.6-3 g/cm^3 with an accuracy better than 0.3%. They can operate at high temperatures of the measured medium – up to 200°C, and are designed for the pipe diameters from 50 to 400 mm and pipe walls thickness up to 12 mm. They can also be constructed in anti-explosive housings.

The prospect for their production in the future looks well and the expected area of the application are chemical, food and mineral processing industries.

2.3. Thickness gauges

There are several types of radioisotope thickness gauges produced in Poland by the Polon-ZOT:

- 38 gauges designed for fast measurements and control of steel sheets have been installed in six steel making and rolling plants. They exhibit a very good accuracy – 1 μm within the range 0.1-4 mm. The measurements are performed using a γ-source Am-241, or a β-X converter with Sr-90.
- Thickness meters for thin Al or plastic foils, paper and cardboard are also offered with a traversing device. Scanning traverses of length up to 3300 mm consist of the frame with driving motors and a movable measuring head. Hence, the gauges can be used for the profile determination and mapping. This group of thickness meters use the β-rays (Pm-147, Kr-85 and Sr-90) absorption method with an ionization chamber used for the detection of transmitted radiation. Measurement range covered by the gauges is from 20 to 800 μm and 250-950 g/m^2 with an accuracy better than 1%.
- Pipe walls thickness gauges are designed for on-line measurements of plastic pipes during the production process. Principle of operation is based on the absorption of γ-rays from Am-241. The instrument can be used for measurements of wall thickness from 2 to 50 mm for plastic pipes of diameters within 50-630 mm. During the measurements, profile of the pipe is shown on a computer display.

In the last years increasing demand for on-line thickness gauges from the industry is observed. This can be explained by the pressure which is borne on the industry to maintain high quality of the final product. The contactless radiation thickness gauges are accurate, reliable and capable to operate in the heavy industrial environment, hence their position on the industrial sensor market is very high.

2.4. Coating thickness gauges

Laboratory coating thickness gauges operating on the principle of β-rays backscattering were designed for fast, non-destructive measurements of metallic and non-metallic coatings. The ranges of the measured thickness depend on the energy of primary β-radiation, and in the case of the determination of Au thickness on a Cu substrate are up to 2 μm for Pm-147, 10 μm for Tl-204 and 20 μm for Sr-90. Their use is limited to such cases where the difference in the atomic numbers between the coating and substrate material is higher than 5. Ten, fifteen years ago there were many such instruments used in industrial laboratories. Competition of the much cheaper devices based on other physical principles (electromagnetic, eddy-currents etc.) caused a considerable decrease of demands on the β-backscattering coating thickness gauges. However, on-line XRF coating thickness gauges (e.g. for Zn or Sn coatings measurements) are still unrivaled. But instead of radioisotope sources, X-ray tubes are commonly used in such installations. Unfortunately, the Polish manufactures of industrial gauges do not use, as yet, X-ray tubes for XRF analysis and coating thickness measurements.

2.5. Nucleonic weighers

Nucleonic belt weighers are designed for non-contact on-line measurements of the bulk materials transported on the conveyors of belt width from 300 to 1000 mm. They were intended for application in the heavy industrial environment. The belt weighers operate on the principle of γ-absorption (Am-241, Cs-137) and the weighing accuracy is claimed to be about 1%. In the 80's the producer of the nucleonic belt weighers has obtained a certificate of the Polish Committee of Standards and Measurements. However, in spite of the relatively high number of the current installations it seems that the industry is less interested in further application of nucleonic weighers. Progress made in design and development of electronic weighers caused that in many cases nucleonic gauges are replaced by cheaper and more accurate electronic devices. The prospect of future application of the nucleonic belt weighers is rather gloom.

2.6. Sulphuric acid concentration gauge

Designed and produced in the Institute of Nuclear Chemistry and Technology these gauges are intended for a continuous, non-contact measurement of sulphuric acid concentration through a pipe-line (Table 2). The hydrogen content is a measure of the acid concentration in the solution, which can be determined using slowing-down neutrons from a Pu-238/Be source. The most suitable concentration range for the instrument is 90-99% H_2SO_4 (Fig. 1). In this range of concentration conductometric devices, as well as methods based on density measurements have a much worse performance. This gauge can properly operate at temperatures of the acid flowing in the pipeline up to 140°C. More than 40 gauges were installed and are used mainly for the automatic control in sulphuric acid production plants. One can say that by now all demands for such gauges from the Polish industry are fulfilled.

Table 2. Neutron gauges of acids concentration

Acid	Concentration %	Pipe-diameter mm	Sensitivity %/%	Accuracy % abs.
H_2SO_4	95-100	108/100	5.1	0.2
	93-98	108/100	4.4	0.2
	70-80	60/54	2.2	0.5
	65-75	57/50	1.7	0.6
HF	65-75	57/50	1.2	0.8
HNO_3	55-65	57/50	2.0	
H_3PO_4	70-80	57/50	1.1	
H_2SiF_6	30-40	66/47	approx. 1	

2.7. Ash in coal monitors

Measurement methods for the ash content in coals, continuous quality monitoring systems (ash and moisture content, calorific value determination) for coals transported on belt conveyors have been elaborated and modernized by the EMAG Centre for almost 30 years. The two on-line systems have found the widest application:

- A system consisting of a radiometric ash monitor based on the measurement of γ-rays from Am-241 backscattered from the coal layer, and a microwave moisture meter based on measurements of the intensity of 9 GHz microwaves reflected from the coal surface. The ash content can be measured within the range 3-50% and moisture content from 2 to 20%. Accuracy of both the measurements is better than 1%. Having determined values of the ash and moisture it is possible to compute the calorific value of the coal transported on the conveyor. About 30 such measuring systems have been installed in the Polish coal mines and coal processing plants.

- A system based on the two-source γ-rays (Cs-137, Am-241) absorption method. The main advantage of this system is that results do not depend on the varying mass and layer depth of the coal. Till now three such systems have been implemented for raw coal quality inspection.

A laboratory radiometric ash monitor can also be used for the determination of sulphur. The X-ray fluorescence method is applied with a Pu-238 source and a proportional counter. The accuracy of ash determination in powdered samples of coal is about 1%.

Coal production in Poland is relatively high - about 120 milion tons in 1997 and a huge majority of the electric power production is based on coal. Hence, it can be expected that in the future demands for industrial gauges designed for inspection of the coal quality will be at least at the same level as today. Since nucleonic gauges are practically unrivaled for the on-line ash measurements their future prospects look quite well.

2.8. Airborne dust monitors

The instruments were developed in the INCT in the 80's and later modernized and are still being produced and installed. Principle of operation is based on the measurement of dust mass collected on a fiber glass filter. The dust is collected when the air sample of known volume is pumped through the filter. The mass of the dust is measured using absorption of β-rays from a Pm-147 source. The instrument operates automatically and needs no attendance for months. Results are stored in the memory and/or can be transmitted through a modem and public telephone line. The range of measurements is from 5 to 5000 $\mu g/m^3$ and the reproducibility about 2% but not less than 2 $\mu g/m^3$. Optionally, the monitor can be fitted with a set of meteorological sensors for the measurement of speed and direction of wind, temperature, humidity and pressure of the air.

The dust monitor is not an industrial gauge, but is intended to measure the degree of industrial pollution. Instruments for the current monitoring of the environmental pollution designed for the operation in monitoring networks are of great importance. The beta absorption airborne dust monitor proved its usefulness for this purpose, therefore its future prospect looks rather well.

2.9. Analyzers

This group of instruments consists of analyzers designed for on-line application in industry and laboratory devices. Their principle of operation is based on X-ray fluorescence excited by such radioisotope sources as Fe-55, Cd-109 or Am-241. Proportional counters are used for the detection of secondary radiation. The industrial analyzer designed by the Polon-ZOT consists of an immersing XRF probe for "in-stream" measurements of Fe, Zn and Pb in a zinc ore processing plant. The laboratory XRF instruments are offered by the Polon-ZOT and the INCT and are very useful for fast, non-destructive analysis and coating thickness measurements in industrial laboratories.

There are several places, where simple analyzers could be applied. It seems that in the future a number of applications will considerably increase when the radioisotope sources will be replaced by an X-ray tube. Analyzers employing radioisotope sources will be preferable in field applications.

All the radioisotope gauges presented above belong to the new generation of measuring devices. They are computerized and are fitted with the data processing and archivization software. An interesting feature of the gauges produced by the Polon-ZOT is the use an ionization chamber for majority of applications. They are very suitable detectors for industrial application due to their robust construction and stability. However, successful using of ionization chambers was possible thanks to a precise I/f (current/frequency) converter of sensitivity about 820 cps/10^{-12} A. The pressurized β and γ ionization chambers and He-3 proportional counters are produced by the Institute of Nuclear Studies. The new producer of the X-ray proportional counters DETRON claims a resolution of its products for the Mn K X-ray below 15%. Radioisotope sealed sources for industrial gauges practically are not produced in Poland. Similarly, as it was said above, the X-ray tubes applicable for industrial gauges are not produced in Poland.

3. TRENDS IN DEVELOPMENT OF RADIOISOTOPE GAUGES

First industrial applications of radioisotope instruments were reported about 50 years ago. As early as in 1957 the number of radioisotope thickness and density gauges installed in the United States was 4000 and increased to 9000 in 1964. In 1961 there were 1465 radioisotope gauges installed in France, 1347 in Germany and 2000 in the United Kingdom [1]. However, it can be supposed that since that time the increase in the number of new installations of nucleonic gauges in industry is much slower.

An interesting question is, how to compare radioisotope gauges developed, say 40 years ago with those recently produced in the developed countries? Which components of the gauges remained unchanged and where the most substantial progress is being observed? It seems that generally, the measuring heads, or measuring probes, are those components of the radioisotope gauge which remained almost in the same shape as forty years ago. Progress in the radiation detectors used in the industrial gauges is not very impressive. Practically, during the last fifty years no new detector applicable in the industrial instruments has appeared on the market. The hopes for non-cooled semiconductor detectors designed for operation in heavy industrial conditions were not realized. The choice of detectors used in the industrial gauges is the same as forty years ago: ionization chambers, gas filled and scintillation counters. Naturally, the progress in technology caused that the performance of modern detectors is in some cases considerably better than that produced in the past, but physical principle of their operation is still the same.

A similar situation can be observed in the field of the radioisotope sources. The choice of the radioactive nuclides applicable in the industrial instruments is limited to a few β, γ and X-ray sources (see e.g. Table 1). However, during the last decade, in some industrial applications the radioisotope sources are superseded by X-ray tubes, which are considered as more safe and their price become comparable with the radioisotope source.

The domain, where the most dramatic progress has been observed and which had a crucial impact on the performance of radioisotope gauges is the electronics. The modern electronics creates almost unlimited possibilities of signal processing. Microprocessor systems or microcomputers, which are included in practically every modern gauge, enable application of sophisticated computational methods to extract useful information from the measured signal or collected data. It may be supposed that in the near future progress in the design and application of the nucleonic gauges will be mainly based on the development and implementation of those methods into the measuring practice.

A good example of such methodology could be the multivariate analysis. It consists of a collection of methods that can be used when several measurements are made on each object in one or more samples. Historically, the bulk of applications of multivariate techniques have been in the behavioral and biological sciences. However, recently interest in multivariate analysis has spread to numerous other fields of investigation [3].

An attempt of using some multivariate techniques in radioisotope gauges was undertaken few years ago [4]. Application of such multivariate techniques as partial least squares regression (PLS) and artificial neural networks for the calibration of some nucleonic gauges will be presented in the next chapters.

4. CALIBRATION OF NUCLEONIC GAUGES

To calibrate a measuring instrument, empirical data and a prior knowledge should be used for determining how to predict unknown quantitative information y from available measurements x via some transfer function [5]. Correct identification of this function, called also the calibration model, is very important, since any incorrectness in the model which is later used for prediction, directly influences the measurement error.

One of the specific feature of nucleonic gauges is a sophisticated process of radiation interaction with matter, as well as the physical effects connected with conversion of the radiation intensity into electrical signals. These effects cannot be satisfactorily described by simple physical models which could be applicable in metrology. It seems that the calibration models of nucleonic gauges should be identified experimentally and a convenient way of their identification is regression analysis. Examples of the calibration models of some nucleonic gauges are presented in Figs. 2a and 2b [6]. It can be seen from the above examples that for most of the nucleonic gauges, their calibration models are linear or non-linear, but can be considered as univariate, since generally they use a single variable to determine the measured quantity. However, in some cases identification of a model using univariate methodology fails, and then methods of multivariate calibration should be tried.

Fig. 3 shows a response from the immersing XRF probe used for "in-stream" measurements of iron, zinc and lead content in slurry. The device is actually operating in a lead-zinc ore processing plant. The peaks of characteristic radiation of Fe, Zn, and Pb excited with Cd-109 and measured with a proportional counter are strongly overlapped. It is not possible to use detectors of better resolution in the severe industrial conditions. But even having all the peaks resolved, some procedures should be developed to cope with the interelement effect.

Other example is the calibration of the XRF gauge designed for the simultaneous determination of thickness and composition of Sn-Pb deposits plated on the printed boards [4, 7]. The measured sample was irradiated with the γ-rays of Am-241. Spectra of the secondary radiation detected by an argon filed proportional counter is shown in Fig. 4. Four interesting area can be observed in the presented spectrum: the Sn L peak of energy 3.5 keV, the Cu K peak of energy 8 keV, the Sn K peak at 25 keV and the area between 9 and 14 keV where Pb L peaks should be present. The Cu K peak overlaps the Pb peaks and the determination of net intensity of the Pb L peaks is very difficult. An attempt at the application of any quantitative method relying on the net peak area and least square fitting to the layer thickness and/or tin content in the layer has failed. In both the mentioned gauges the calibration problem was solved using a multivariate approach.

5. MULTIVARIATE APPROACH

Multivariate calibration means the determining how to use many measured variables $x_1,x_2,...x_m = \mathbf{x}$ simultaneously for quantifying some target variable y [5]. For instance, variable **x** could be a vector corresponding to the entire spectrum of measured radiation (Figs. 3-4) and the target variable could be measured quantity (e.g. thickness or concentration of an analyte). In the multivariate calibration, if **y** is a vector of dependent variable from n observations and **X** is a matrix of m variables from n observations (n spectra of m channels), the linear regression model looks like:

$$\mathbf{y} = \mathbf{X}\mathbf{b}_K + \mathbf{f} \qquad (1)$$

where: $\mathbf{b}_K$ - vector of m regression coefficients; **f** - vector of residuals.

Least squares solution of the above equation (by the multiple linear regression - MLR) is equal:

$$\mathbf{b}_k = (\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T\mathbf{y} \qquad (2)$$

The MLR model when used for the whole spectrum variables presents two main problems:

- Estimation of **b** can be accomplished if the number of observation n is sufficiently higher than the number of the variables (channels) m.
- Matrix $\mathbf{X}^T\mathbf{X}$ is being inverted, so the columns of **X** should not be intercorrelated.

To solve equation (2) and to avoid problems connected with the MLR approach, the biased regression methods such as principal component (PLS) could be used. Their principle is to compress the matrix data

$$\mathbf{X} = \{\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_m\} \qquad (3)$$

into a set of a latent variables, called also components or factor scores:

$$\mathbf{T} = \{\mathbf{t}_1, \mathbf{t}_2, ..., \mathbf{t}_a\} \qquad (4)$$

where a << m. In other words, the matrix **X** is decomposed into the sum of outer products of vectors called loadings **(p)** and scores **(t)**:

$$\mathbf{X} = \mathbf{t}_1\mathbf{p}_1^T + \mathbf{t}_2\,\mathbf{p}_2^T + ... + \mathbf{E} = \mathbf{T}\mathbf{P}^T + \mathbf{E} \qquad (5)$$

where **E** is the matrix of residuals not explained by the above model.

The score vector **(t)** represents the correlation between the objects (samples) whereas the loading vector **(p)** represents the correlation between the variables [8].

Having matrix **X** decomposed into a few (a) components **t** it is easy to find a relationship between the vector of the dependent variable **y** and the score matrix **T** and then to compute **b**, being used to predict the value of y_p from the measured spectrum $\mathbf{x}_p$.

$$y_p = \mathbf{x}_p \cdot \mathbf{b} \qquad (6)$$

Selection of the optimal number of components (a), included into the calibration model, is very important since it determines prediction ability of the model. As more dimensions are included, the model may be overfitted owing to the addition of higher rank components containing more noise. The overfitted models fit well to the calibration data but have worse predictive abilities [5]. Selection of the optimum number of components can be accomplished by internal cross-validation. The principle of leave-one-out cross-validation is such that from a given set of n reference samples the calibration is performed using n-1 samples and the $\hat{y}_{i,CV}$ value for the object not included into the calibration set is predicted. This process is repeated a total of n-times until each sample has been left once. The sum of squared differences between the reference y_i and predicted $\hat{y}_{i,CV}$ values, called RMSECV (root mean squared error of cross-validation) is a measure of predictive ability of the model. A reasonable choice for the optimum number of components would be that which gives the minimum RMSECV.

$$\mathrm{RMSECV} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_{i,CV})^2} \qquad (7)$$

Formal tests for predictive ability of a PLS model with a given number of dimensions can be found in the literature [9].

Another method of model validation is using an independent set of k reference samples (not participating in calibration) and compute the root mean square error of prediction (RMSEPr)

$$\mathrm{RMSEPr} = \sqrt{\frac{1}{k}\sum_{i=1}^{k}(y_i - \hat{y}_{i,pr})^2} \qquad (8)$$

where:

k - number of samples in the prediction set

y_i - reference value

$\hat{y}_{i,pr}$ - value predicted from the model

A quantity showing how well a chosen model for a particular set of calibration samples fits the reference data is called RMSEE (root mean square error of estimation).

$$\mathrm{RMSEE} = \sqrt{\frac{1}{n-a-1}\sum_{i=1}^{n}(y_i - \hat{y}_i)^2} \qquad (9)$$

Multivariate calibration can also be used for identification of non-linear models [10]. In such cases, the inner relation between the dependent variable y and the latent variable t for each component is approximated by a non-linear function, such as a polynom or a spline [11].

Since the middle of the last decade an increasing drive towards the application of the artificial neural network (ANN) has been observed. One of the fields when ANN offer a powerful set of tools is multivariate calibration of sophisticated measuring systems [12]. Sometime both the multivariate calibration methods are combined: PLS loadings are used as weights of the neurons in the hidden layer of the ANN.

Computation leading to identification and validation of the multivariate model can be performed using available software packages, e.g. [13]. However, it seems that one of the important problems emerging in the multivariate calibration of nucleonic gauges is to find physical interpretation of the computed results. It should be always kept in mind that multivariate data analysis which is the base of multivariate calibration, tells about calibration data structures and correlation patterns but it does not tell the name of the processes that generated then [8].

6. APPLICATION

Application of the multivariate calibration will be presented on the three following examples: the measurement of thickness and composition of the Sn-Pb layers, the determination of ash in black coal, and the measurement of coating thickness of the nickel on the iron substrate. In all the considered examples X-ray fluorescence was used as the measurement methodology.

6.1. Thickness and composition of Sn-Pb layers

A set of 24 reference samples of Sn-Pb coating thickness ranging from 2 to 9.5 μm and Sn content in the layer within the range 60-81% was used for the calibration and prediction testing. X-ray spectra (Fig. 4) from 16 samples were used to construct a calibration model and 8 of them to test the prediction ability of the model under development.

Spectra of the first two PLS loadings **p** and predictors **b** computed for the coating thickness measurement and determination of the Sn content in the layer are presented in Figs. 5-6. They show the contribution of individual parts of the X-ray spectrum (Fig. 4) in the value of the predictor **b** used for the determination of thickness and composition from the calibration model. It can be seen, that for the coating thickness the most important part of the spectrum is the Cu K peak, whereas for the Sn content its contribution is negligible. On the other hand, the Sn and Pb L peaks as well as Sn K play the most important role in the Sn content determination. The latter is in good agreement with the qualitative examination of the spectra presented in Fig. 4. However, using multivariate decomposition of the calibration matrix one gets a quantitative relationship between the radiation intensity collected in the individual channels and the measured parameters (thickness and composition of Sn-Pb layer).

The score plot presented in Fig. 7 reveals that the first component represents variability of the responses from the calibration samples, caused by the changes of the Sn-Pb coating thickness whereas the second PC is responsible for the variability of Sn content in the layer. This also agrees well with the pattern shown in Fig. 4 where it can be seen that the changes in coating thickness much more influence the intensity of the registered radiation than the variability of the Sn content in the layer.

The same data were used to develop an ANN calibration model [14]. The network was learnt successively for each of the parameters (thickness and Sn content). Number of neurons in the hidden layer varied from 1 to 4. Two ways of NN training were applied:

1. preset weights and thresholds of neurons in the hidden layer were random variables ranging from -1 to 1.
2. weights of the hidden layer neurons were chosen as the loadings computed for the PLS regression for the same set of the calibration samples.

Prediction abilities of both the ANN and PLS models have been computed and results are presented in Tables 3 and 4. The models were tested using a set of samples (not included into the calibration set) but for the PLS model a cross-validation technique was also applied. It is seen that in the case of coating thickness measurements the RMSEPr value is considerably lower for the ANN model than for the PLS but in the determination of Sn content the ANN model gives generally poorer results. However, when the PLS loadings are used as weights of the neurons in the hidden layer, RMSEPr for Sn content improves and learning process in this case becomes much faster.

Table 3. Root mean square errors of estimation, cross-validation and prediction for PLS regression

		a = 1	a = 2	a = 3	a = 4	a = 5
Thickness	RMSEE µm	0.63	0.42	0.21	0.10	0.05
	RMSECV µm	0.61	0.46	0.36	0.41	0.41
	RMSEPr µm	0.65	0.52	0.35	0.40	0.41
Tin content	RMSEE %Sn	8.82	2.05	1.20	0.72	0.43
	RMSECV %Sn	8.29	2.40	2.42	2.59	2.63
	RMSEPr %Sn	5.20	1.31	0.83	0.90	1.10

Table 4. Root mean square errors of prediction (RMSEPr) for different number neurons (S1) in the first layer. ANN model

		S1 = 1	S1 = 2	S1 = 3	S1 = 4
Random weights	Thickness µm	0.41 0.45	0.31 0.27	0.33 0.27	0.35
	Tin content %Sn	3.14	2.28	1.81 2.06	3.26
Weights of the first layer as loadings from PLS	Thickness µm	-	0.25 0.28	0.27 0.28	-
	Tin content %Sn	-	1.20 1.27	1.10 0.82	-

It seems that better results of the coating thickness measurement obtained for the ANN calibration model can be explained by the fact that the relationship between the intensity of registered radiation and the coating thickness is non-linear. It can be expected that the ANN calibration model computed for the tansigmoid transfer function should exhibit better prediction ability than the linear PLS model.

Cross-validation of the PLS model yields a local minimum at three latent variables (Table 3) whereas no more than two would be expected, because there are only two processes influencing the calibration data system - variable coating thickness and Sn content. It can also be explained by the fact that an extra latent variable is required to model the non-lineanties existing in the data set.

One can observe also that number of neurons (S1) in the first layer of the ANN corresponds to the number of components in the PLS model. For S1 = 4 some overfitting can be seen, and the same effect can be noticed for the number of PLS factors higher than 4.

6.2. Determination of ash in coal

Possibility of using X-ray fluorescence and scattering of the low energy X-ray for measurement of ash concentration in coal was reported in the literature many years ago [15]. The weakness of this method is the influence of the variable iron content in the measured sample on the intensity of backscattered radiation. This effect can be observed in Fig. 8, where the spectra of 28 coal samples with ash content ranging from 2 to 30% are presented. It is seen that for samples with a high iron content (peak at 6.4 keV), a "valey" in backscattered radiation (15-20 keV) can be observed. It is possible to overcome this effect using multivariate calibration.

The spectra from Fig. 8 were used as the calibration data set to compute PLS models. Two models were computed: the first, using the original spectra and the second, using the corrected spectra, where in the area of backscattered radiation, instead of count-rates in the individual channels their reciprocal values were taken to the model. The spectra of the PLS predictors **b** for the first and second component, for the original and corrected spectra are shown in Fig. 9. It is seen that in both the cases intensity of Fe K radiation has a significant contribution to the model.

Table 5. Root mean square errors of estimation (RMSEE) and cross-validation for PLS models. Measurement of ash content in coal

		a = 1	a = 2	a = 3	a = 4	a = 5
Original	RMSEE %	4.48	1.99	1.64	0.89	0.57
spectra	RMSECV %	4.55	2.09	1.89	1.70	1.78
Corrected	RMSEE %	6.00	1.31	1.11	0.97	0.54
spectra	RMSECV %	6.16	1.49	1.29	1.10	1.16

Mean square errors of estimation and cross-validation are presented in Table 5 [14]. A local minimum of the RMSECV is observed for the models consisting of four components. However a minimal RMSECV value for the corrected spectra (1.1%) is about 50% lower than that for the original spectra (1.7%), which confirms advisability of the applied correction.

The same data sets (original and corrected) were used for computation of the ANN calibration, but no significant improvement as compared with the PLS model, was observed.

6.3. Measurement of Ni thickness on Fe substrate

The spectra of 13 reference samples of Ni coating deposited on a Fe base are shown in Fig. 10. Thickness of the Ni layer varied from 1 to 14 μm and their XRF spectra were collected in 70 channels. The measurements were performed using a Cd-109 X-ray source and an argon-filled proportional counter. It can be seen that the Fe K and Ni K peaks are strongly overlapped. Moreover, the relationship between the intensity of the registered Ni K or Fe K peaks and the coating thickness is non-linear.

Both the linear and non-linear PLS regressions were used for the calibration and the obtained results are presented in Table 6 [16]. In the non-linear PLS the second and third degree of polynomial regression spline was used as inner relation [11]. It can be seen that the linear models give rather poor results. The results obtained for non-linear models are considerably better, however, increasing the degree of polynom and/or the number of knots of the used regression spline causes an increase of RMSECV value, whereas RMSEE remains at the same level. It is a typical overfitting effect [5] and the possibility of its occurrence should always be taken into consideration, especially in the non-linear PLS and ANN models [17].

Table 6. Results of measurements of Ni coating on steel substrate obtained with linear and non-linear PLS calibration

RMSEE µm	RMSECV µm	Number of components	Degree of polynom/Number of knots in spline
0.65	0.85	1	Linear model
0.34	0.68	2	Linear model
0.29	0.35	1	2/0
0.27	0.55	1	3/0
0.27	0.36	1	2/1
0.27	0.57	1	3/1

7. DISCUSSION OF THE CALIBRATION RESULTS

Multivariate calibration can be used in the gauges giving a response in the form of a vector. In other words, it can be applied in such cases, where spectrometric signal is used, or signals from many sensors or detectors are collected. Its use in spectrometric radiometric gauges is advantageous especially in those cases, where useful information is not sufficiently selective and is distributed over the whole spectrum. This means that it may be successfully used even when the peaks in the spectrum overlap. Moreover, this calibration procedure allows also to compensate the interelement effect, when used in XRF analyzers.

Physical interpretation of some PLS parameters is important, since it can provide a new insight into the methodology used, thus allowing a better understanding of measuring process. It is dangerous to apply a statistical predictor if the user does not understand what it means.

Non-linearity between the measured quantity and the intensity of registered radiation can be included in the calibration model either by increasing the number of PLS components or by applying non-linear models. Also artificial neural networks have proved their applicability for development of the multivariate calibration models. However, using the ANN method for calibration, a possibility of finding physical interpretation of computed parameters is lost.

Multivariate, compared with the univariate calibration method exhibits also an important feature - creates the possibility of detecting a sample as an outlier. One of the methods of outliers detection is analyzing the score plots (Fig. 7) for first two or higher rank components.

In the PLS calibration model, variation in the data matrix **(X)** is approximated by **TP,** where **T**, spans all possible types of systematic factors: e.g. concentrations, coating thickness, interferences and non-linearities. Hence, the measuring system can be calibrated for a single factor, assuming other factors influencing data matrix as interferences. It has been shown, that in the case of the Sn-Pb layers, the system can be calibrated for the Sn content without a knowledge of the layer thickness, providing that the thickness is properly spanned in the calibration set. Generally it should be noted, that all the phenomena that vary in the target population, must be spanned in the calibration set and described in the calibration model [5].

Application of the methods of multivariate analysis is not only limited to the calibration. These methods can be also used for interpretation of the results obtained from the measuring devices as well as for the pattern recognition or image processing [18].

8. CONCLUSIONS

There are more than thousand radioisotope gauges installed in the Polish industry. They belong to the new generation of measuring devices and their performance fully satisfy their industrial users. It seems that in the near future, the number of installed level, thickness and density gauges, as well as ash and airborne dust monitors together with industrial analyzers will be kept at least at a similar level as today. The number of installed nucleonic belt weighers and laboratory coating thickness gauges rapidly decreases.

One of the direction of development in the field radioisotope gauges is the application of the multivariate analysis for the calibration and data treatment. Some studies of this subject showed that the multivariate calibration gives very promising results and can create new applications of the radioisotope gauges, particularly in those cases where spectrometric methods of X and γ-ray are employed.

Acknowledgements

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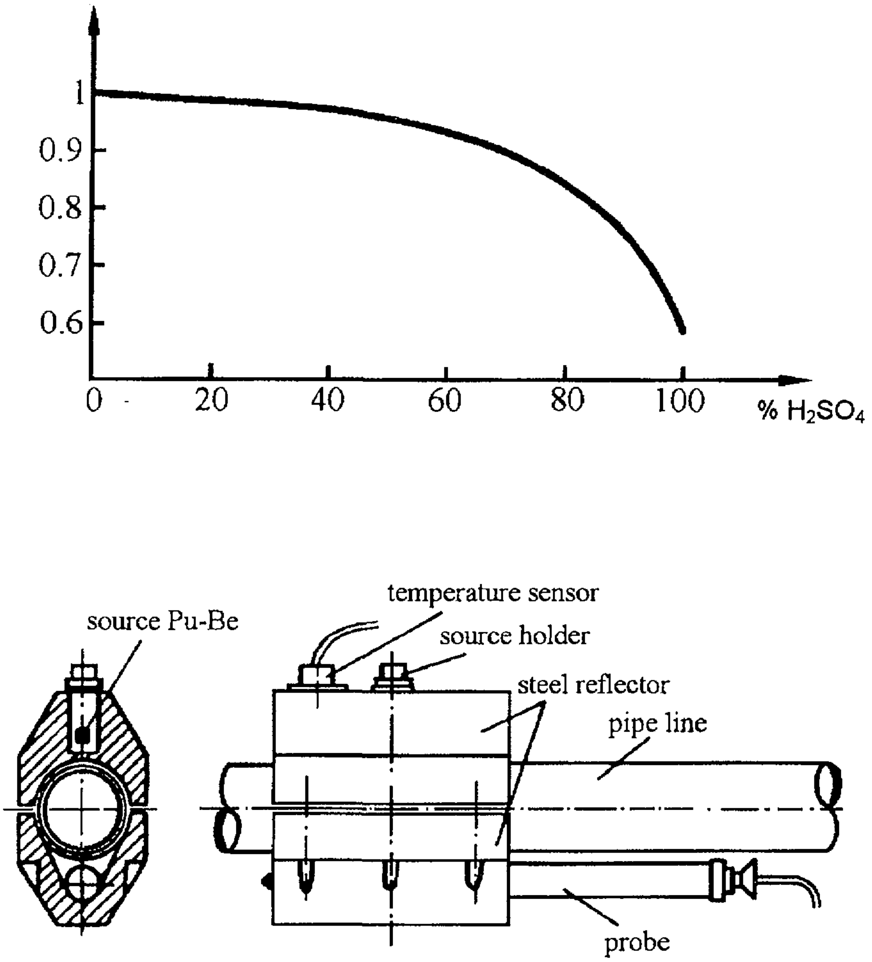

Fig. 1. Relative thermal neutrons flux density against acid concentration and measuring head of MSK-4 gauge.

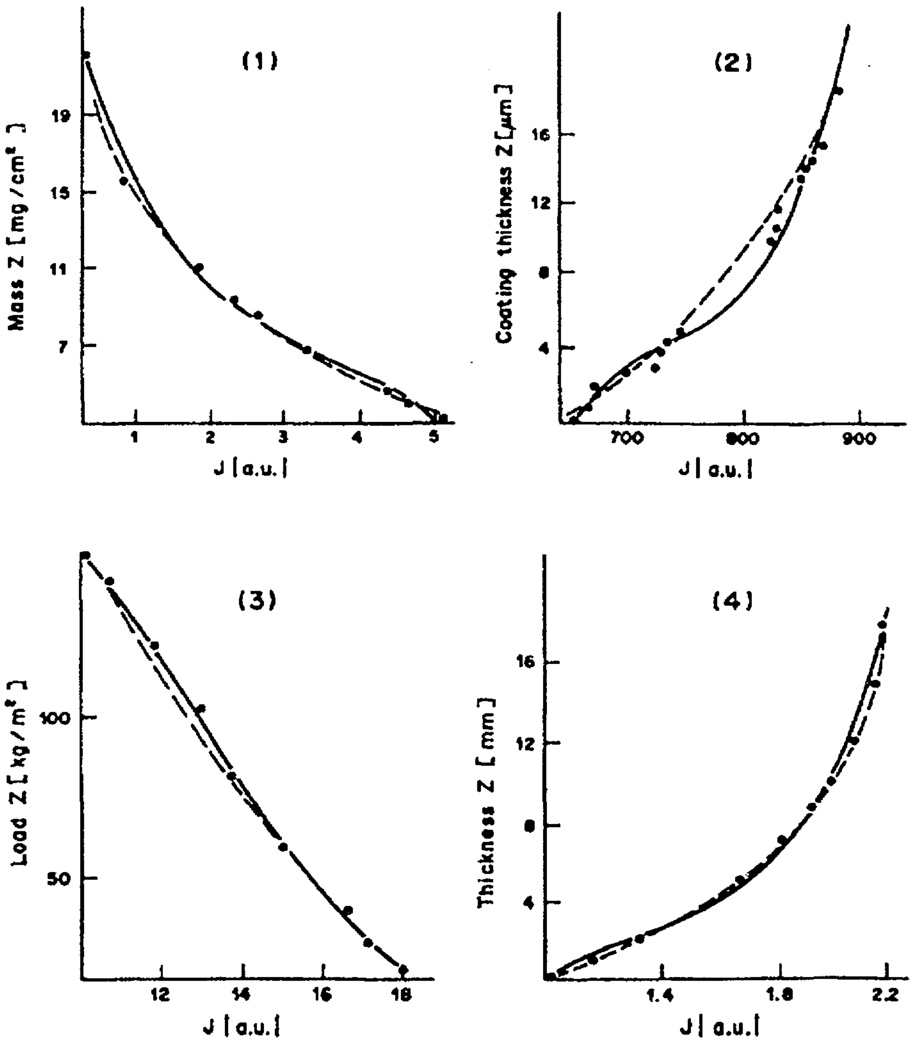

Fig. 2a. Models of calibration procedures of some radioisotope gauges.
(1) β-transmission; (2) β-backscattering; (3) γ-transmission; (4) γ-backscattering.

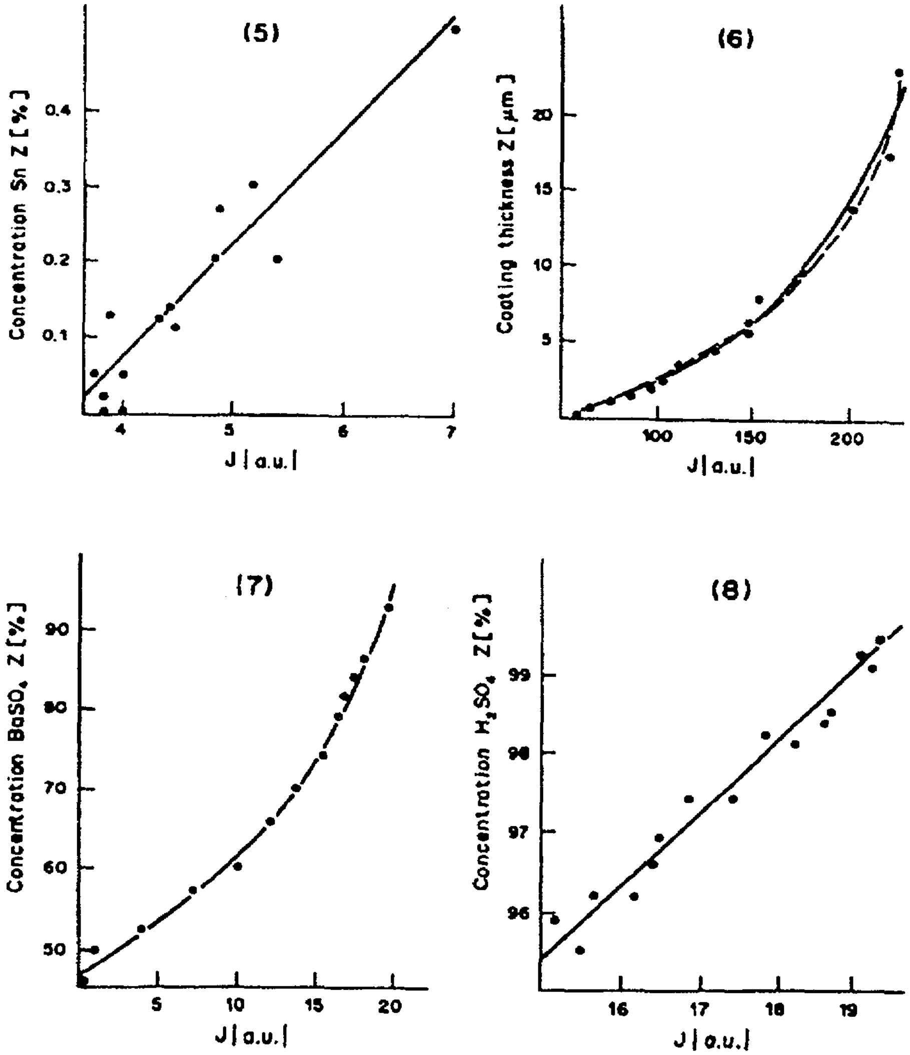

Fig. 2b. Models of calibration procedures of some radioisotope gauges. (5) XRF (analysis); (6) XRF (coating thickness); (7) γ-selective absorption (reversed scale); (8) n-scattering (reversed scale).

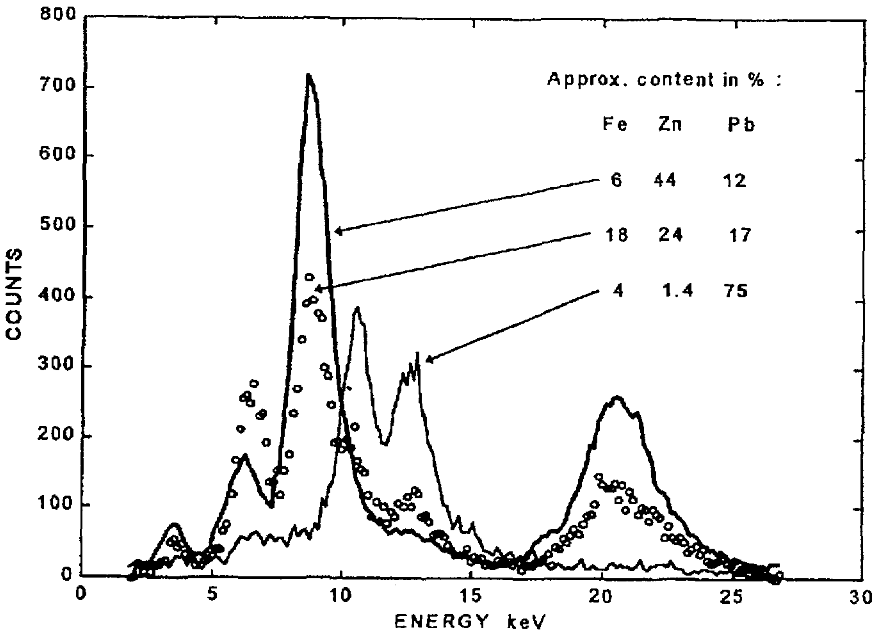

Fig. 3. Secondary X-ray spectra from three samples measured by the immersion probe installed in a zinc-lead ore processing plant. Source - Cd-109, detector - Ar proportional counter. (By courtesy of the POLON-ZOT).

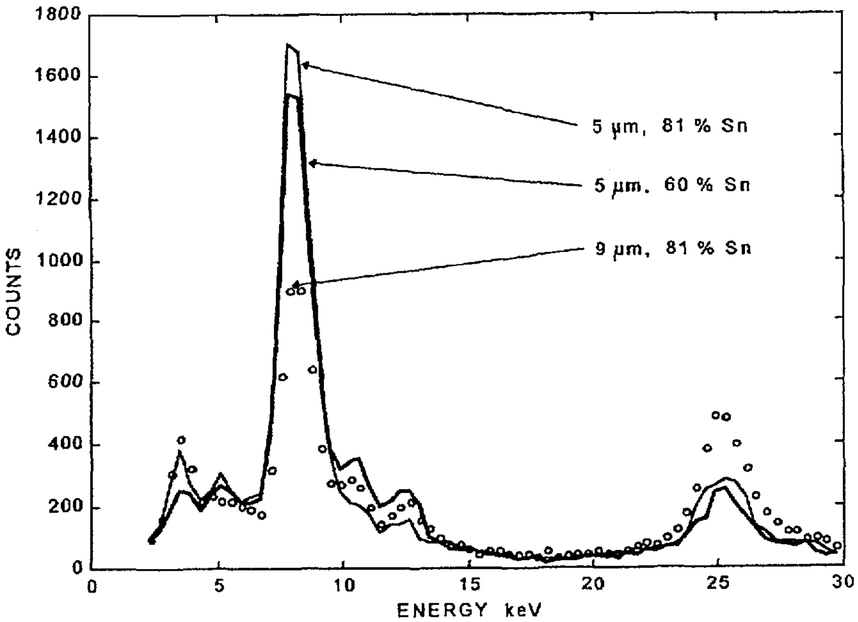

Fig. 4. Secondary X-ray spectra from three samples of different thickness and composition of Sn-Pb layers plated on printed board.

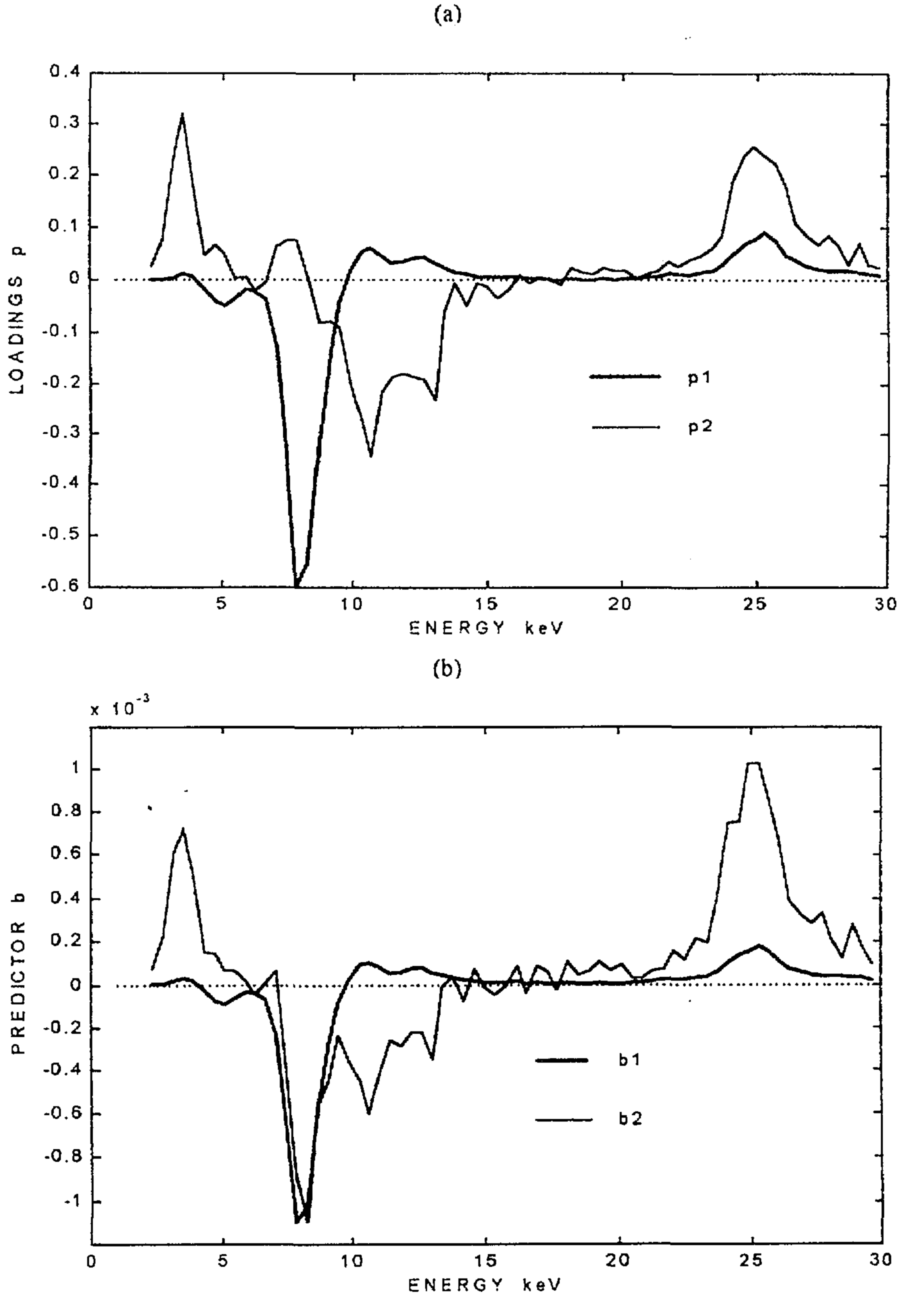

Fig. 5. PLS loadings (a) and predictors (b) for the first two principal components. Calibration of Sn-Pb coating thickness.

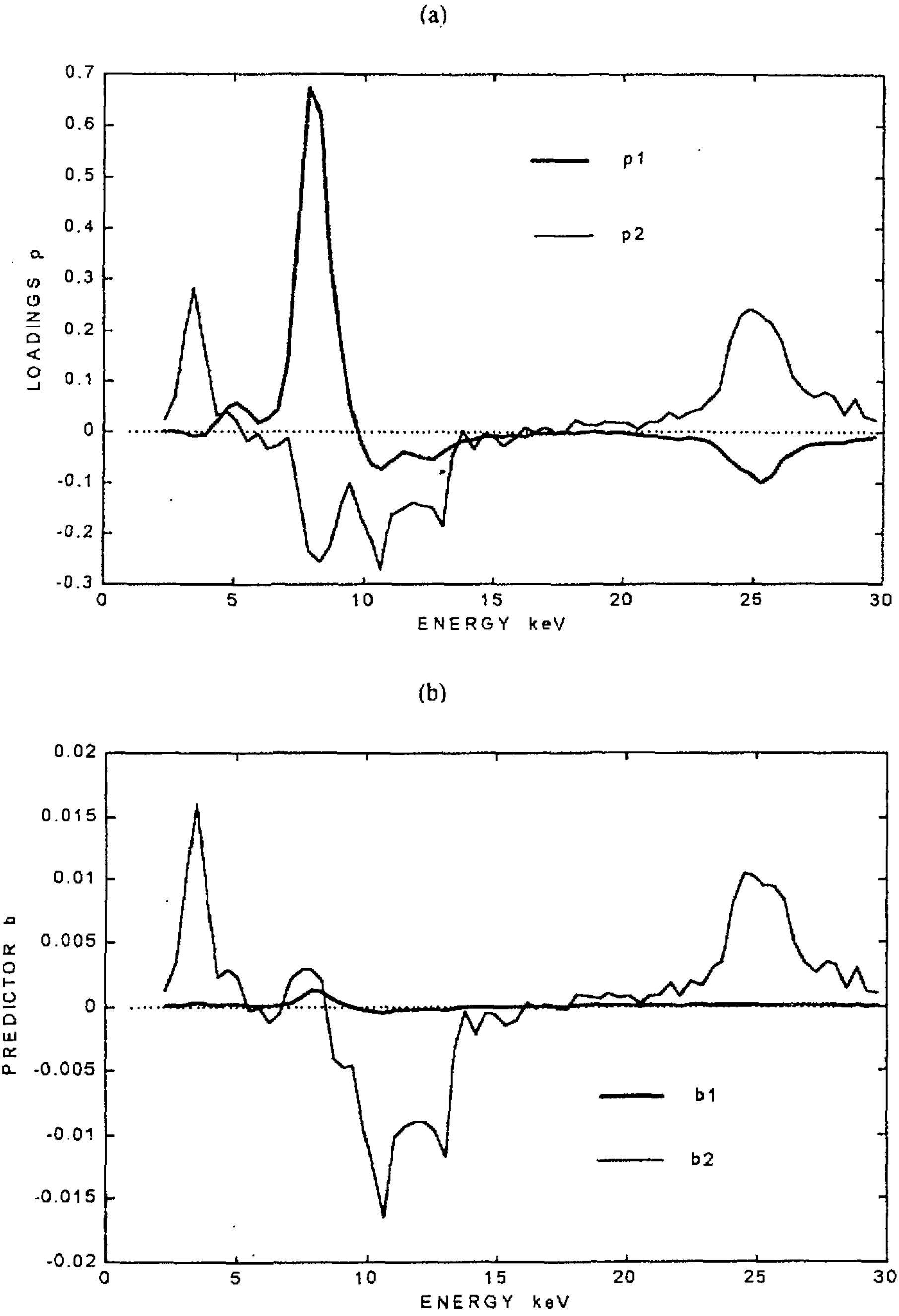

Fig. 6. PLS loadings (a) and predictors (b) for the first two principal components. Calibration of Sn content in layer.

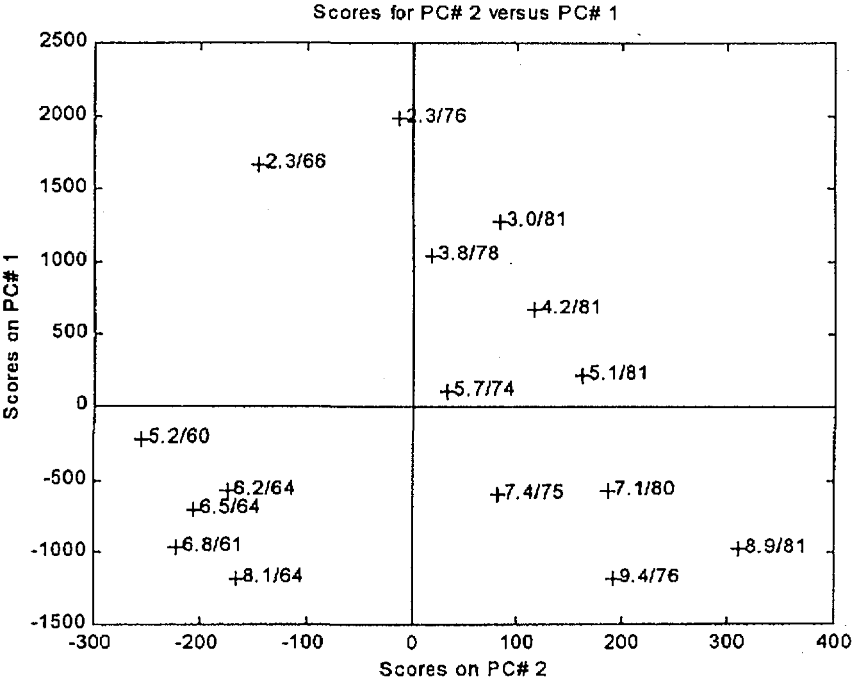

Fig. 7. Scatter plot of the two first scores for the set of calibration samples. First number left of the cross shows the coating thickness in µm and the second number - Sn content in the layer in %.

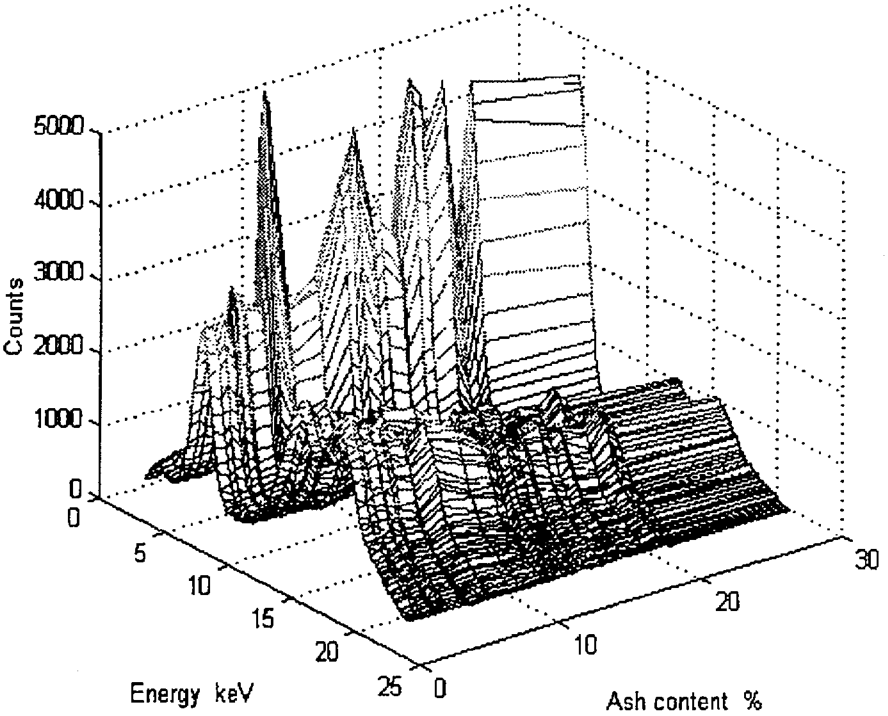

Fig. 8. Spectra of the secondary X-rays from 28 powdered samples of black coal. Source - Pu-238, detector - Ar proportional counter.

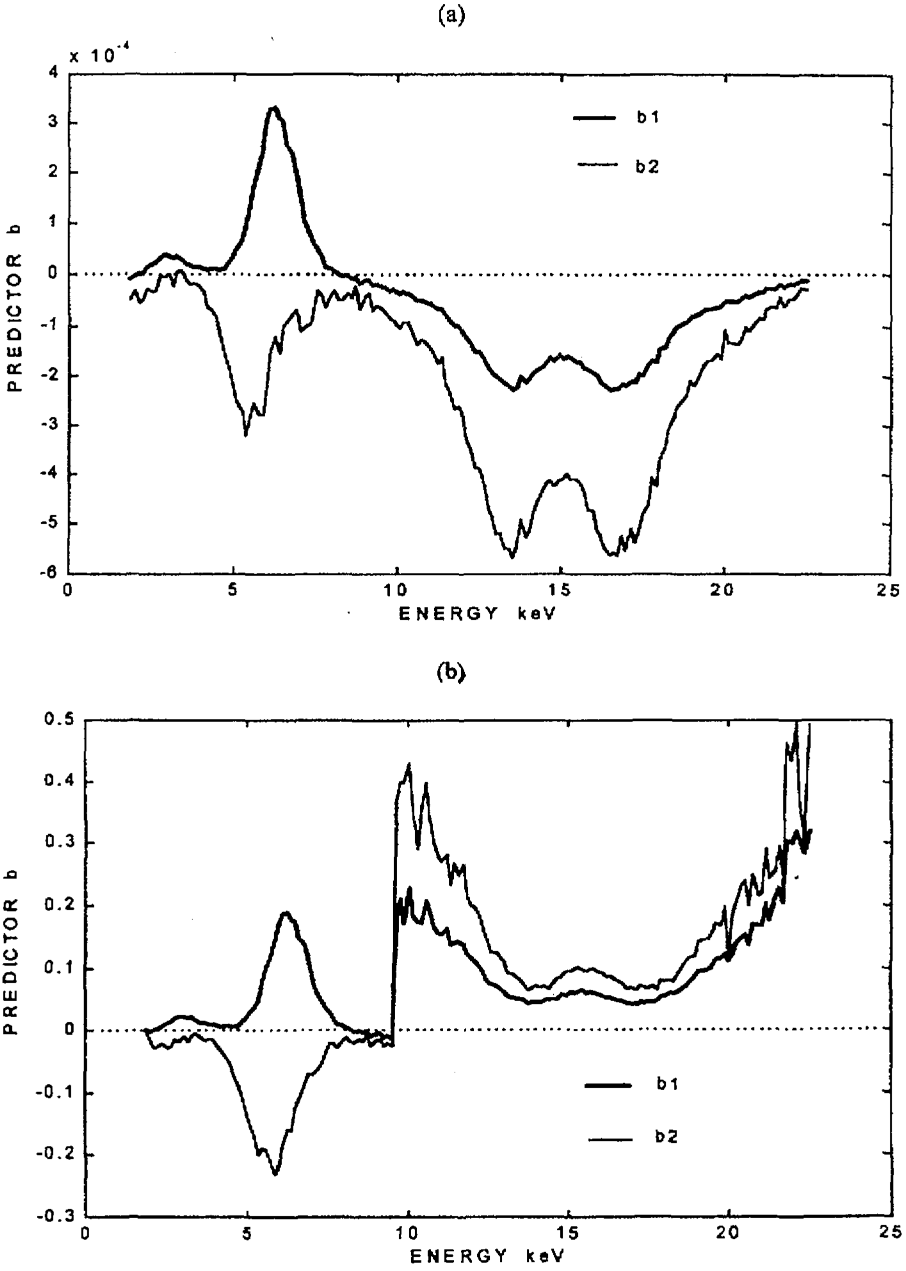

Fig. 9. Predictors b for the first and second principal components for the original (a) and corrected (b) X-ray spectra of the coal samples from Fig. 7. In corrected spectra, reciprocal value of counts corresponding to the scattered radiation is taken to the model.

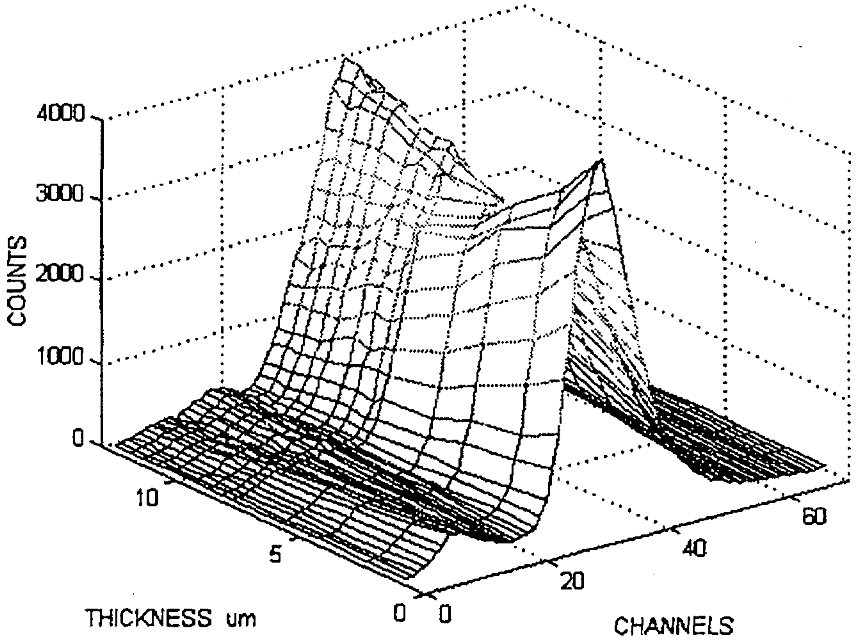

Fig. 10. XRF spectra of a set of Ni/Fe reference samples.
Source - Cd-109, detector - Ar proportional counter.

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