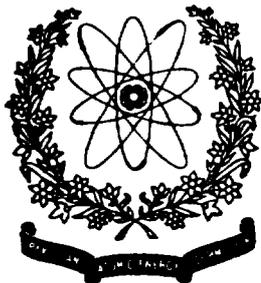PK960'0210

FABRICATION OF SO$_2$ PREPARATION SYSTEM AND CALIBRATION OF PINSTECH SULFUR STANDARD FOR ^{34}S/^{32}S MASS SPECTROMETRIC ANALYSIS

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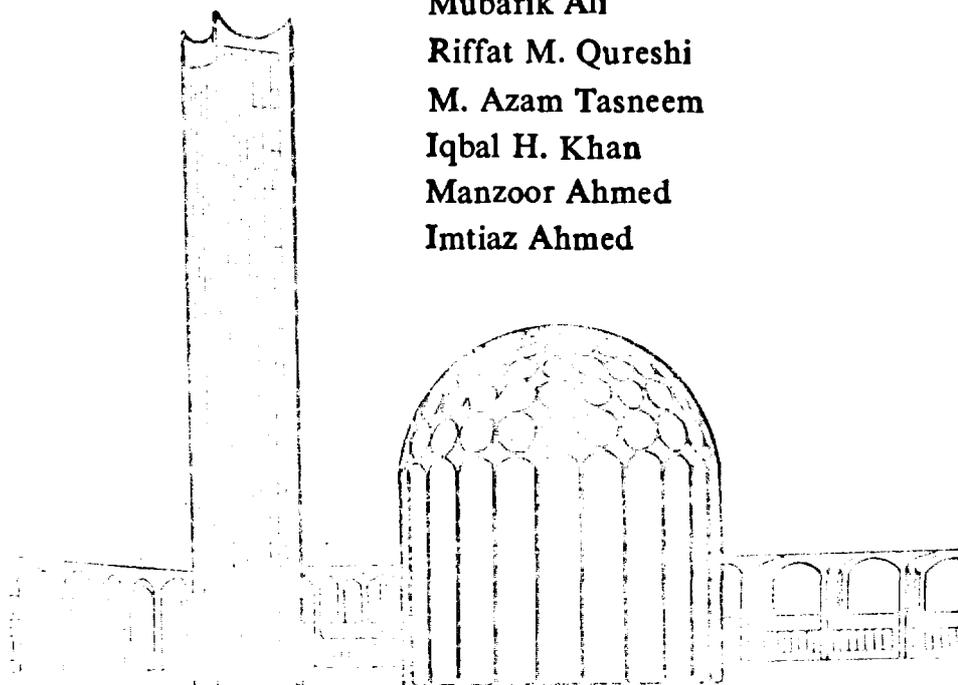Pakistan Institute of Nuclear Science & Technology
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CONTENTS

ABSTRACT

This report describes the fabrication and standardization of operation procedures of a "SO_2 preparation system" used for the extraction of sulfur dioxide gas from sulfur minerals (aqueous sulfate, elemental sulfur, and sulfides) for sulfur isotope ratio measurements on a gas source mass spectrometer for hydrological, geological and environmental applications. SO_2 preparation procedure as described by Fumitaka Yanagisawa and Hitoshi Sakai (1983) is adopted with some modifications. A chemically pure $BaSO_4$ powder is chosen as PINSTECH Sulfur Standard (PSS-1) for routine laboratory ^{34}S analysis. PSS-1 is calibrated against the International Atomic Energy Agency (IAEA) standard Cannon Diablo Troillite (CDT) using the NBS-127 sulfur standard. $\delta^{34}S$ values of PSS-1 as analyzed at PINSTECH and Institute fur Hydrologie, Munich are found to be 14.58 ± 0.07 ‰ CDT (n=6) and 14.59±0.15 ‰ CDT (n=2) respectively. NBS-127 is $BaSO_4$ powder from the National Bureau of Standards, USA and has been calibrated against CDT. Interlaboratory comparison of various standards is also documented. Using this system, the reproducibility of sulfur isotope ratio measurements is better than ± 0.2 ‰ (n=10).

1. INTRODUCTION

Sulfur bearing natural compounds possess different isotopes of sulfur in different proportion. Approximate abundances of four stable isotopes of naturally occurring elemental sulfur e.g. ^{32}S, ^{33}S, ^{34}S and ^{36}S are 95.02, 0.75, 4.21 and 0.02 % respectively [Hoefs, 1987]. Two isotopes ^{32}S and ^{34}S are exploited in most of the studies due to their favourable abundances in nature. Variations of sulfur isotopes in compounds provide a powerful method of investigation in various disciplines of geosciences. In hydrological applications, $\delta^{34}S$ values can be used to formulate hypotheses on the geochemical processes undergone by the dissolved sulfur compounds, and with caution, as an index of water. This is a characteristic common to all environmental isotopes which are part of a dissolved compound, and not part of the water molecule itself [Fritz & Fontes, 1980].

Isotopic variations of sulfur compounds can be used to identify groundwater origin and to study its geochemical and hydrological history. The prerequisite is that the isotopic composition range of sulfur compounds be characteristic for each of the water bodies taking part in a given groundwater system, so that they can be identified by the isotopic label. Ideally, the isotopic ratio determination of dissolved sulfur compounds should be complemented by that of water.

Sulfur isotopes are also used to determine the origin of sulfide ore-deposits. It is of great help to distinguish between ore-deposits formed as a result of igneous activity and those that are of sedimentary origin. Freshly deposited sediments are depleted in ^{34}S compared to marine sulfates. Sulfur associated with igneous rocks derived from upper mantle have $\delta^{34}S$ values close to zero. Pyrite mineralization has been found in some parts of Pakistan and ^{34}S would provide evidence of any hydrothermal activity and uranium bearing zones [Hoefs, 1987].

Isotopic study of sulfur can be used in source identification of atmospheric particulates arising from different sources. Smelting of magmatic sulfides introduces SO_2 into the atmosphere with $\delta^{34}S$ values near zero per mil (‰) whereas lead-zinc recovery from sedimentary ores tends to release gaseous sulfur compounds with greater enrichments in $\delta^{34}S$. Emission from power plants have a wide range in isotopic composition, dependent upon the source of fuel. Rain water sulfate is depleted in ^{34}S with respect to seawater sulfate, the effect being more pronounced in industrial areas. Rain and snow contain sulfate from a number of sources. Sea spray sulfates should have a $\delta^{34}S$ value near +20 ‰, assuming that only mechanical transport takes place. Sulfate arising from the oxidation of biogenic H_2S or volcanic gases is comparatively depleted in ^{34}S. Values greater than +20‰ can be found in precipitation where industries such as sour-gas plant operations utilize isotopically heavier sulfur compounds [Fritz & Fontes, 1980].

Another aspect of assessing the capability of sulfur isotopes in environmental studies is determining the extent to which the isotope abundances are altered in natural processes. Source identification becomes difficult if large isotopic selectivities arise in ensuing processes [Fritz & Fontes, 1980].

Sulfur and its compounds may threaten the environment if their concentration exceed the permissible level. Some damages are caused by direct mechanism and other by indirect mechanisms. Sulfur and its chemical derivatives interact biochemically with building material and vegetation directly, affect flora and fauna by causing change in soil or aquatic ecosystems indirectly. In the case of forest damage, it is possible that both direct and indirect mechanisms are involved [Commission of European Communities, 1983].

Acid rains, linked to the burning of fossil fuels, inflict damages upon forests, lakes and cities. This damage continues and problems have become even more menacing. Today fossil fuels make up about 90 % of world's commercial energy, and this heavy use is at the root of some of the most serious environmental problems which the world faces today. The smockstack exhausts of coal-fired power plants, in addition to others, contain sulfur oxides and nitrogen oxides. PINSTECH is continuously monitoring the sulfur contents of rain at various sites through the measurement of ^{34}S.

This report deals with the local fabrication of sample preparation system for the conversion of sulfates/sulfides to SO_2 gas for mass spectrometric analyses of $^{34}S/^{32}S$ ratios. The report gives a brief review of the methodology of SO_2 preparation; different techniques and their relative merits, and details of the technique adopted & modified at PINSTECH. The standardization of preparation procedures, the calibration of standards and some applications of ^{34}S have also been given in the report.

2. ^{34}S MEASUREMENT TECHNIQUES

Most reported studies have examined ^{32}S and ^{34}S because of their more favourable abundances and the extensive use of SO_2 gas for mass spectrometric determinations. Very little additional information would be gained in hydrological investigations by measuring the ratios of the other isotope pair.

There are two techniques for the mass spectrometric analysis of $^{34}S/^{32}S$. These include the measurement of sulfur isotopic ratios through SF_6 and SO_2 gases, and both are based on different sample preparation methods. Relative merits and demerits of each are described in the following sections.

2.1. Measurement Through SF_6

In recent years SF_6 has gained favour for sulfur analysis on mass spectrometer. Puchelt & Kulterud, [1970] originally developed this technique. This gas is extremely stable and is without any memory effect. Furthermore, fluorine is monoisotopic and major ion species SF_6 yields the abundances desired without corrections. However, the preparation technique such as fluorination and purification is time consuming. The new reference standards still have to be calibrated using this preparation technique.

Perhaps, due to complexity in the preparation of SF_6 , most of the commercial mass spectrometers, so far, are based on SO_2 method for ^{34}S analysis.

The design of the ^{34}S mass spectrometer developed is initially based on SO_2 technique. At a later stage, it is intended to incorporate some modifications to increase the mass spectrometer resolution for SF_6 analysis, as much better resolution is needed due to its higher mass-to-charge ratio (compared to SO_2).

2.2. Measurement through SO_2 Gas

SO_2 is the most commonly used gas for mass spectrometric analysis of ^{34}S. The main advantage of this technique is that SO_2 is readily prepared. The preparation is simple and less time consuming.

However, SO_2 has disadvantages in sulfur isotope analyses. Firstly, it is a sticky gas in vacuum systems, particularly in the presence of traces of water. This property creates memory effect which is minimized by continuous heating of the ion source and inlet system. However, corrections still may be necessary for this memory effect. Secondly, large correction factors are involved due to ^{18}O contribution to mass 66 as $^{32}S^{16}O^{18}O^+$ and $^{34}S^{16}O^{16}O^+$ are not resolved in typical isotope abundance mass spectrometer. These oxygen isotope corrections coupled with SO_3 production require consistency in the combustion procedure. Further, it is also important to minimize the productions of sulfur trioxide and sulfates during the preparation of samples. [Hoefs, 1987; Fritz & Fontes, 1980].

Accurate analytical techniques for sulfur isotope determinations on small samples are desirable for experimental investigations of natural sulfur isotope variations. Previously, most sulfur bearing samples were converted to $BaSO_4$ which was then reduced to $H_2 S$ by graphite at 1,000°C [Rafter, 1959] or the HI-H_3PO_2-HCL reducing solution described by Thode et.al (1961). The $H_2 S$ was then converted to Ag_2S which was oxidized to SO_2. Alternately, $BaSO_4$ was thermally decomposed to SO_2 under vacuum after mixing with reagents such as $NaPO_3$ [Halas and Wolacewicz 1981: Halas et al., 1982] and Cu_2O plus

SiO_2 [Celeman and Moore, 1978]. These methods generally required a relatively large amount of the original material.

Direct combustion of Ag_2S and other sulfide minerals to SO_2 has been carried out using O_2 [Thode et al.,1961], O_2-N_2 mixtures (Sakai and Yamamoto, 1966), and solid oxidants such as PbO [Vinogradou et al.,1956] , V_2O_5 [Gavelin et al., 1960; Ricke,1964],CuO [Grinenko, 1962; Fritz et. al, 1974] or Cu_2O [Robinson and Kusakabe, 1975]. In these combustions, the yield of SO_2 was often as low as 75% [Ueda & Krouse, 1986].

Laborious preparation of $BaSO_4$ from sulfur compounds in impure samples can be omitted by evolving H_2S from the original material with Kiba reagent [Sasaki et. al., 1979]. Ueda and Sakai (1983) developed on in vacuo Kiba reduction procedure to extract small quantities of sulfide and sulfate sulfur separately. However, this technique requires at least two hours per sample [Ueda & Krouse, 1986].

Many laboratories use both Ag_2S oxidation and $BaSO_4$ decomposition methods. However, the oxygen isotope composition of SO_2 from both techniques can cause differences in the computed $\delta^{34}S$ value of more than one per mil because masses 64 and 66 are usually collected in sulfur isotope determinations. Whereas the former consist of one species $^{32}S^{16}O_2$, the later has two main contributions $^{32}S^{16}O^{18}O$ and $^{34}S^{16}O_2$ which are not resolved in low resolution mass spectrometers .

Influence of the oxygen isotope ratio of SO_2 due to inconsistency of $^{18}O/^{16}O$ ratio, was not corrected in the above mentioned techniques. For accurate $\delta^{34}S$ determinations, constant $^{18}O/^{16}O$ abundance ratio in SO_2 is required. Therefore, V_2O_5-SiO_2 mixture for $BaSO_4$ decomposition used by Yanagisawa and Sakai (1983) was adopted to the sulfate and sulfide minerals. The method provides SO_2 with constant $^{18}O/^{16}O$ ratios among the samples and as such a consistent correction factor for the effect of Oxygen Isotope Composition of SO_2 can be applied. In order to maintain the reproducibility of ± 0.1 ‰ in sulfur isotope determination, $^{18}O/^{16}O$ ratio must be uniform within ± 1 ‰.

3. SO₂ PREPARATION SYSTEM

3.1. Apparatus

The essential parts of the apparatus used for extraction of SO_2 gas are shown in figures 1 & 2. It essentially consists of a quartz reaction chamber and pyrex glass vacuum line in which the SO_2 produced in the reaction chamber, is collected and transferred to the gas ampoule for subsequent analysis on the mass spectrometer. A two stage rotary pump and a mercury diffusion pump, connected in series, produce high vacuum in the vacuum line and reaction chamber. Two pirani gauge heads are mounted to monitor the vacuum.

The reaction chamber is about 26 cm long and its outer diameter is 9 mm (fig. 1a). The chamber is closed at one end while through the other end (grounded cup) it is attached to the vacuum line using an o-ring. A mixture of sulfate or sulfide, V_2O_5 and SiO_2 is put in another smaller closed end quartz tube which is packed with a wad of quartz wool at the open end. This is then placed at the bottom of reaction chamber.

A round furnace having the temperature between 750°C to 800°C is mounted at the middle of reaction chamber having copper turnings there. Another furnace which can provide temperature in the range of 900°C to 1050°C is mounted at the lower end of reaction chamber. The SO_2 collection line consists of two U-tube cold traps, a manometer and the sample ampoule.

3.2. Furnace: Design parameters and fabrication

Furnace was locally designed (fig. 1c) depending upon the requirements of the line and geometry of the reaction chamber. Design parameters are given below.

Material: Alumina tube and Kanthal wire
(o.d. 1mm & s.w.g. 18)
Effective length: 12 cm
Inner diameter (alumina tube): 2.5 cm
Max. temperature range: upto 1200°C
Working temperature: 750 to 800°C
Length of stable temperature region: $\approx$ 4 cm

The Kanthal wire was wrapped around the alumina tube in such a way that the range of constant temperature extends towards open ends. It was then surrounded by a thick paste of MgO coarse powder and sodium silicate. Material for the fabrication of the furnace was selected keeping in view the requirement of work and the availability of material. Alumina and Kanthal wire can easily bear temperature upto 1200°C. Alumina tube with wrapped Kanthal wire was enclosed in S.S. hollow cylindrical chamber. Space between the tube and chamber was filled with asbestos rope and grounded MgO. Filling material was sealed by S.S. plates at both ends of the furnace to contain the toxicity of asbestos. Before its routine use, the furnace was baked in the open air by slowly increasing the temperature upto 1200°C.

4. SO_2 EXTRACTION PROCEDURES

Finely powdered sample in the form of sulfate or sulfide equivalent to 40 μ mole of sulfur (or 10 mg of $BaSO_4$ / $\approx$4 mg of ZnS) is thoroughly mixed with V_2O_5 (100mg) and SiO_2 (100 mg) [Ueda & Krouse, 1986] in an agate pestle and mortar. This intimately

ground mixture is placed in a small quartz tube of about 6 mm o.d. A tuft of quartz wool is inserted in the open end of this tube. Then it is transferred into the reaction chamber. Another wad of quartz wool is placed about 2 cm above the inner tube. This double-tube-arrangement ease the introduction of sample and cleaning of the tubes for re-use.

The reaction chamber is then heated upto 450°C for about 30 minutes by placing it in the aluminum block (fig.1b) in open air to remove any organic contaminants [Yangisawa & Sakai, 1983]. Two grams of metallic copper gauze or turnings covering about 2 cm length is placed in the middle of the reaction chamber. The reaction tube is connected to the sample preparation line through a right-angled stopcock adopter as shown in figure 2.

The reaction chamber is evacuated (upto the order of 10^{-2} mbar) by opening stopcocks 3, 6, 7, 9 and the stopcock of adopter. The copper metal is heated upto 800°C by the furnace (fig.1c) to remove the oxide coating and volatile contaminants. Stopcocks nos. 3, 6, 7 and 9 are opened and the line is evacuated before opening the right angled stopcock. The line is continuously evacuated till the out-gassing is appreciably reduced and vacuum stability is achieved (at 10^{-2} mbar).

Lower portion of the reaction chamber containing the reactants is heated by another furnace (shown in figure 1d). The temperature of this furnace raised above 900°C gradually. After the temperature of the reactants is reached close to 500°C, stopcock no. 6 is closed. Evolution of SO_2 starts at about 600°C and reaches its maximum value near 750°C for sulfates [Yanagisawa & Sakai, 1983]. However, sulfide minerals start producing SO_2 at 750°C with maximum evolution near 950°C [Ueda & Krouse, 1986].

After 6 minutes of the closure of stopcock 6, the trap 1 is immersed in liquid nitrogen. Stopcock 6 is then slowly opened to pump all the non-condensable gases. This delay of six minutes minimizes the bumping of the mixture. This also increases the transit time of SO_3 over the heated copper turnings helping in its conversion into SO_2. Sulfur dioxide produced in the reaction chamber is collected in trap 1 for about 20 minutes. Liquid nitrogen at trap 1 is replaced with an acetone slush bath (temperature -95°C) and the trap 2 is immersed in liquid nitrogen in order to transfer SO_2 into the trap 2. The portion of the line from stopcock numbers 6 to 9 is evacuated, stopcock 7 is closed and the liquid nitrogen at trap 2 is removed. Pressure of the collected SO_2 is measured by the manometer. This gas is finally collected in a sample ampoule by immersing it into liquid nitrogen. Ensure that stopcock 9 is closed before opening the stopcock no. 7. SO_2 collected in the sample ampoule is again purified before removing the ampoule for mass spectrometric analysis.

Sulfate or sulfide of the sample reacts with V_2O_5 at more than 600°C under vacuum to form SO_2, O_2 and SO_3. The later is converted into SO_2 by its reduction with copper metal. X-ray diffraction analysis of the solid reaction products reveals that compounds like $BaV_{12}O_{30}$, V_2O_4, V_2O_5 are formed when $BaSO_4$ is thermally decomposed to form SO_2.

Quartz powder in the mixture do not take part in the reaction upto 1000°C but acts as a buffer between the sulfate/sulfide and oxides in the molten mixture to uniform the isotopic composition of oxygen. V_2O_5 is added to lower the decomposition temperature of $BaSO_4$ in the mixture from 1400°C to about 900°C. Pure V_2O_5 melts at 600°C and it acts as a flux which dissolves $BaSO_4$ and yields the following products [Yanagisawa & Sakai, 1983]:

$$BaSO_4 + 6\ V_2O_5(melt) = = = = > BaV_{12}O_{30} + 1/2\ O_2 + SO_3$$
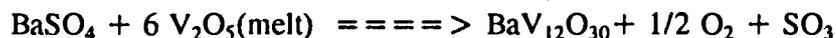
Excess SiO_2 and V_2O_5 both lower SO_2 yield. For this reason, the V_2O_5 / SiO_2 weight ratio of unity has been considered to be the most appropriate. Whereas a ratio of $(V_2O_5 + SiO_2)$/ $BaSO_4$ of 6:1 provided a good SO_2 yield at a low temperature, a ratio of 20:1 was preferred to assure uniformity of oxygen isotope composition of the SO_2.

Partial pressure of oxygen at site of $BaSO_4$ decomposition is controlled by V_2O_5-V_2O_4 equilibrium. This is evident by the presence of $BaV_{12}O_{30}$ in the reaction product. Copper plays dual role in this reaction. Firstly it reduces SO_3 to SO_2 and secondly it maintains the low partial pressure of oxygen to give the high yield of SO_2 [Yanagisawa & Sakai, 1983].

5. CALIBRATION OF ISOTOPIC MEASUREMENTS

5.1. Standards

The following standards were used in the calibration of procedures for SO_2 gas preparation and routine measurements of [34]S / [32]S stable isotope ratios and convertion to δ [34]S values :

PSS-1 = Laboratory Internal Standard namely: "PINSTECH Sulfur Standard-1" (Chemically pure $BaSO_4$ powder).

CDT = Cannon Diablo Troillite (a reference standard, available from the International Atomic Energy Agency, Vienna, Austria).

NBS-127 = $BaSO_4$ powder from the National Bureau of Standards, USA.

MSS-3 = Laboratory internal standard of the Institute for Thermal Spring Research, Okayama University, Japan.

PS2 = Working standard; SO_2 gas from a commercial gas cylinder.

5.2. Reproducibility of Isotopic Measurements

Using the procedure described in section 4, sulfur dioxide gas samples were prepared from $BaSO_4$ of the International standard; NBS-127 and the PINSTECH internal laboratory standard; PSS-1. These SO_2 samples were measured on the modified GD-150 mass spectrometer against the working standard namely; PS2.

The isotope ratio (mass-66/mass-64) measurements (expressed as $\delta\ ^{66}S_m$ ‰) of standards NBS-127 and PSS-1, carried out over a period of about three months, are summarized in Table I.

Table-1

Run No.	Analysis date	$\delta\ ^{66}S_m$ (‰)	
		NBS-127	PSS-1
1	10-03-92	18.63	13.42
2	11-03-92	19.12	13.75
3	12-03-92	18.75	13.43
4	16-03-92	18.61	13.41
5	14-05-92	18.90	13.66
6	28-05-92	18.90	13.58
7	04-06-92	18.80	13.56
Mean:		18.82 ± 0.18	13.54 ± 0.13

The analytical reproducibility of the standards NBS-127 and PSS-1 is better than 0.2 ‰. Each pair of run number was measured at least three times in order to ensure the stability of the mass spectrometer. The difference was reproducible at about 0.1 ‰. This indicates that reproducibility of sample preparation line and that of the mass spectrometric measurements is acceptable in view of the isotopic differences of natural materials. and compounds.

5.3.   Calibration of Internal Laboratory Standard

The $\delta^{34}S$ values of PSS-1 versus CDT were calculated using the following equations [Halas,1985 & Craig, 1957].

$$^{PSS-1}\delta_{PS2}\ ^{34}S\ =\ 1.09\ ^{PSS-1}\delta_{PS2}\ ^{66}S$$

1.09 is used as a correction factor for oxygen isotope ratio of the sulfur dioxide and to convert $\delta^{66}S$ into $\delta^{34}S$.

$$^{PSS-1}\delta_{NBS-127}\ ^{34}S\ =\ \frac{(^{PSS-1}\delta_{PS2}\ ^{34}S\ -\ ^{NBS-127}\delta_{PS2}\ ^{34}S)\ 1000}{(1000\ +\ ^{NBS-127}\delta_{PS2}\ ^{34}S)}\qquad \text{and}$$

$$^{PSS-1}\delta_{CDT}\ ^{34}S\ =\ ^{PSS-1}\delta_{NBS-127}\ ^{34}S\ +\ ^{NBS-127}\delta_{CDT}\ ^{34}S\ +\ ^{PSS-1}\delta_{NBS-127}\ ^{34}S\ \times\ ^{NBS-127}\delta_{CDT}\ ^{34}S\ \times\ 10^{-3}$$

$^{NBS-127}\delta_{CDT}\ ^{34}S$ has been assigned the value + 20.32 ‰ by IAEA.

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The delta values of internal laboratory standard calculated using the above equations for various sets are given in Table II.

Table II

$^{PSS-1}\delta_{CDT}{}^{34}S$
14.62
14.52
14.61
14.64
14.47
14.52
14.66

Mean: **14.58 ± 0.07 ‰**

The data show that our measurement is in an excellent agreement within the internationally acceptable limit of standard deviation of ± 0.1 ‰.

5.4. Interlaboratory Comparison of Standards:

It was considered helpful to get analyzed our internal laboratory standard PSS-1 from well reputed laboratories of the world dealing with the sulfur isotope measurements. Institute for Thermal Spring Research, Okayama University Japan and IAEA (Vienna) were requested to analyze PSS-1. IAEA got the analysis done from a well reputed laboratory in GSF-Munich. At the same time, the NBS-127 standard and the internal laboratory standard MSS-3 of the Institute for Thermal Spring Research, Okayama University Japan were analyzed at PINSTECH. Results are summarized in Table III.

Table III

Standard/ (country)	Laboratory/ address/ country	Analysis date	$\delta^{34}S$ ‰ CDT	
			single values	mean
PSS-1/ (Pakistan)	PINSTECH Nilore, ISLAMABAD/ Pakistan	March to June, 1992	14.62 14.52 14.61 14.47 ˙14.52 14.66	14.58±0.07 (n= 6)
	Institute fur/ Hydrologie/ GSF, Munich/ Germany	January,1992	14.56 14.61	14.59±0.04 (n= 2)
	Institute for Thermal Spring Research / Okayama University / Japan	July, 1991	15.30 14.98	15.14±0.23 (n= 2)
MSS-3/ (Japan)	PINSTECH Nilore, ISLAMABAD/ Pakistan	13-21 August, 1991	3.47 3.24 3.13 3.64	3.37±0.23 (n= 4)*
NBS-127 (USA)	PINSTECH Nilore, ISLAMABAD/ Pakistan	13-21 August, 1991	20.21 20.00 20.84 21.26	20.58±0.58 (n= 4)**

* Actual value of MSS-3 = 3.5 ‰ CDT.
** Actual value of NBS-127 = 20.32 ‰ CDT.

Results for the standard PSS-1 as measured at Munich and PINSTECH are in good agreement with each other. Also, the $\delta^{34}S$ values of the standards: NBS-127 and the MSS-3 as measured at PINSTECH agree well with the actual values quoted in the literature [Fritz & Fontes,1980; Yanagisawa & Sakai, 1983].

6. APPLICATIONS

Reproducible $\delta^{34}S$ values for the PINSTECH sulfur standard PSS-1 standard are obtained using the developed SO_2 preparation system. The overall accuracy of SO_2 preparation on the extraction system and isotopic measurements on mass spectrometer is better than 0.2 ‰ CDT which is within the required limits for application of sulfur isotopes as a tracer for environmental, geological and hydrological applications.

The calibration of PSS-1 with respect to the international standard CDT is very precise and in good agreement with its isotopic composition determined at IfH-GSF/Munich through IAEA. The SO_2 gas preparation procedures are also verified in view of the intercomparison of MSS-3 and NBS-127 at PINSTECH.

Table-IV

Sample type/ (area)	Mineral analyzed	Sample No.	$\delta^{34}S$ (‰ CDT)
Aqueous	Barium	RD-24	0.27
sulfate/	Sulfate	RD-25	0.21
		RD-26	4.55
(Rechna		RD-29	13.42
Doab)		RD-47	7.17
		RD-73	3.37
		RD-74	3.49
		RD-114	5.91
		RD-115	5.66
Sulfur minerals/			
Gilgit	Galena	G-1	-7.15
Kashmir	Galena/ Pyrite	T-1	+11.45
Kashmir	Pyrite/ Chalco- pyrite	B-21/2	+11.20

The SO_2 preparation system is now in routine operation for preparation of samples for ^{34}S isotopic analysis at the mass spectrometer. Todate $\delta^{34}S$ distribution has been determined on aqueous sulfate samples for waterlogging & salinity studies in Rechna Doab

(hydrological application) and on some sulfide minerals from Gilgit and Kashmir for the evaluation of their origin (geological application). Typical ^{34}S data of these samples is given in Table IV.

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REFERENCES

Coleman, M.L. and Moore, M.P. (1978), Direction reduction of sulfates to sulfur dioxide for isotope analysis, Anal. Chem. 50, 1594-1595.

Commission of the European Communities (1983), Acid rain. A review of the phenomenon in the EEC and Europe; Published by Gradam and Trtotman Limited, U.K.

Craig, H. (1957), Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of CO_2. Geochim. Cosmochim. Acta 12.

Fritz, P. and Fontes, J. Ch.(1980), Handbook of environmental isotope geochemistry, vol. 1. Elsevier scientific publishing company, Amsterdam-Oxford-New York.

Fritz, P., Drimmie, R.J.and Nowicki, V.K. (1974), Preparation of sulfur dioxide for mass spectrometer analyses by combustion of sulfides with copper oxide, Anal. Chem. 46, 164-166.

Gavelin, S., Purwel, A. and Ryhage, R. (1960), Sulfur isotope fractionation in sulfide mineralization. Econ. Geol., 55, 510- 530.

Grinenko, V.A. (1962), The preparation of sulphur dioxide for isotope analysis. Zn. Neogran. Khim.7, 2478-2483.

Halas, S. (1985), On bias in ^{34}S / ^{32}S data obtained using SO_2 gas in mass spectrometry. Proceedings of an advisory group meeting IAEA, Austria (Vienna,1987).

Halas, S. and Wolacewiz, W.P. (1981), Direct extraction of sulfur dioxide from sulfates for isotope analysis, Anal. Chem. 53, 686-689.

Halas, S., Shakur, A. and Krouse, H.R. (1982), A modified method of SO_2 extraction from sulfates for isotopic analysis using $NaPO_3$. Isotopenpraxis 18, 433-436.

Hoefs,J. (1987), Stable isotope geochemistry(Minerals and rocks;9) Springer-Verlag-Berlin-Heidelberg-New York-London-Paris-Tokyo.

Rafter, T.A. (1959), Sulphur isotopic variations in nature, Part-1 the preparation of sulphur dioxide for mass spectrometric analysis, Anal. Chem. 42, 1451-1453.

Ricke, W. (1964), Praparation von Schwefeldioxid zur Massenspektrometrischen Bertimmung des Schwefel-Isotopen-Verhaltnisses ($^{34}S/^{32}S$) in naturlichen Schwefelverbindungen. Z. Anal. Chem. 199, 401-413.

Robinson, B.W. and Kusakabe, M. (1975), Quantitative preparation of sulfur dioxide, for $^{34}S/^{32}S$ analyses, from sulfides by combustion with cuprous oxide, Anal. Chem. 47, 1179-1181.

Saski, A., Arikawa, Y. and Falinsbee, R.E.(1979), Kiba reagent method of sulfur extraction applied to isotope work, Chishitsu Chosasho Geppo 30, 241-245.

Sakai, H. and Yamamoto, M. (1966), Fractionation of sulfur isotopes in the preparation of sulfur dioxide, An improved technique for the precision analysis of stable sulfur isotopes, Geochem. J.1, 35-42.

Thode, H.G., Monster, J. and Dunford, H.B. (1961), Sulphur isotope geochemistry, Geochim. Cosmochim. Acta 25, 159-174.

Ueda, A. and Krouse, R.H. (1986), Direct conversion of sulfide and sulphate minerals to SO_2 for isotope analyses, Geochem. J. 20.

Ueda, A. and Sakai, H. (1983), Simultaneous determination of the concentration and isotope ratio of sulfide, and sulfate-sulfur and carbonate carbon in geological samples, Geochem. J. 17, 185-196.

Vinogradov, A.P., Chupakhin, M.S., Grinenko, V.A. and Trofimov, A.V. (1956), Isotopic composition of sulfur in relation to the problem of the age of pyrites of sedimentary genesis, Geokhimiya 1956, 96-105.

Yanagisawa, F. and Sakai, H. (1983), Thermal decomposition of barium sulfate-vanadium pentaoxide-silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements, Anal. chem. 55, 6.
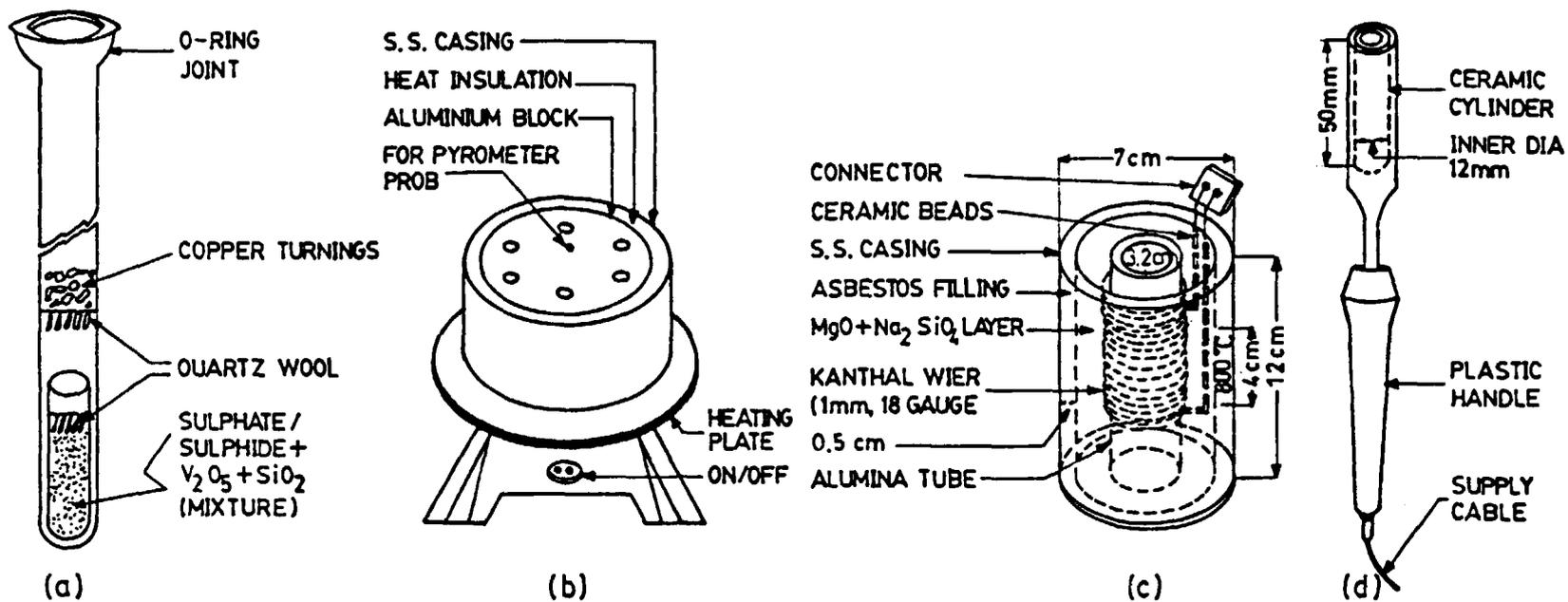
FIG.1: a) Reaction chamber, b) Heating block for degassing, c) Furnace 800°C, d) Furnace for 900–1000°C temperature

FIG·2 : THE VACUUM LINE FOR THE PREPARATION OF SO_2