

Figure 5. Comparison of melting and freezing points measured on the NBS "specific heat standard" sample (second run specimen), for different values of $(t_B - t_S)$. The solid straight line was fitted to the experimental points by using the least-squares approximation method. The equilibration point thus obtained is 122.38_2 °C.

of melting, systematic errors due to heat conduction were effectively cancelled, if the average of the melting and freezing points is considered.

To perform the transformation reversal, the SPRT was withdrawn from its well and a stream of cool dry nitrogen was blown into the well. The gas flow rate and the time of cooling could be experimentally adjusted to defined values in order to lower the block temperature by the desired amount. For instance, 10 L/min for 4.5 min were necessary to cool the block about 4 K. Subsequently, the thermometer was reintroduced and the block current readjusted to keep its temperature constant. Typically, after 18 min the reversal was complete and a stable freezing transformation was started.

These results are summarized in Table III, where negative Δt values refer to freezing points. All freezing point determinations in this table were obtained for $F = 1$, using Taylor and Rossini's procedure.

Using the foregoing considerations, we defined an "ideal" equilibrium point by means of an interpolation between a melting point and its subsequent freezing point. As seen in Table III, all the melting/freezing pairs have nearly symmetrical conditions, so that any uncertainty in every determination is taken into account with the same weight, but opposite sign, for both types of transformation. This is not the case of the extrapolated melting points of Table II. There

the final values are more affected by systematic and random errors in the experimental points.

From Table III we can draw the following conclusions: (a) Equilibrium points agree with the corresponding extrapolated melting points of Table II to better than ± 0.02 K. (b) The results of Table III, second run, reflect the difference in nominal purity between NBS-SRM 350 and NBS "specific heat standard". This last, when converted to a temperature difference according to the procedure of Schwab and Wichers (7), accounts exactly for the difference of 14 mK in the equilibrium point. (c) Considering all measurements carried out with the NBS "specific heat standard" sample in the second run (i.e., taking into account also the melting points of Table II not considered in Table III), a remarkably good correlation results, irrespective of whether the points come from a melting or a freezing experiment, as shown in Figure 5. The resulting equilibrium point (122.38_2 °C) is very well in agreement with the corresponding entry in Table III.

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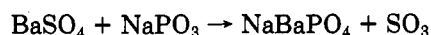
Direct Extraction of Sulfur Dioxide from Sulfates for Isotopic Analysis

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A convenient method of extraction of sulfur dioxide from natural sulfates (BaSO_4 , SrSO_4 , and CaSO_4) for sulfur isotopic analysis is described. A sulfate is reacted with NaPO_3 under vacuum at 850 °C; SO_3 thus obtained is then reduced to sulfur dioxide on copper heated to 750 °C. It has been experimentally shown that the reaction takes place with complete yield and provides very good reproducibility of measurements despite a remarkable variation in ^{18}O content of analyzed sulfates. The long-term reproducibility of $^{34}\text{S}/^{32}\text{S}$ ratios is about 0.05 per mil.

There are only a few methods known for production of sulfur dioxide from sulfates for isotopic analysis (1-3). The latter which entails the reduction of sulfates by cuprous oxide and silica seems to be simple and versatile. In this paper we propose an alternative method, which follows the reaction



at a temperature of 850 °C. This reaction of barium sulfate with sodium metaphosphate was described by Erdey and Paulik in a paper on quantitative analysis of sulfates (4).

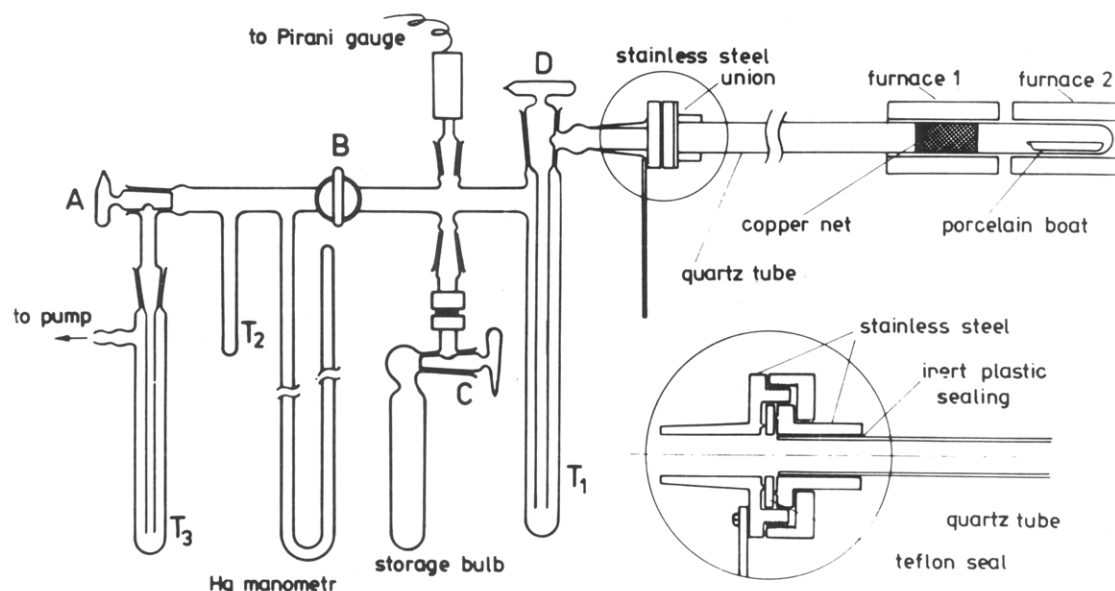


Figure 1. Apparatus for production of sulfur dioxide.

In contrast to the procedure described previously (4), our reaction takes place under vacuum instead of atmospheric pressure. As a result some advantages appear: (i) the decomposition reaction of sulfur trioxide



is enhanced; (ii) the reaction temperature is significantly decreased; and (iii) the sample preparation time is shorter.

EXPERIMENTAL SECTION

Apparatus. The apparatus used is similar to that applied previously to the preparation of SO_2 from sulfides. It is a vacuum line essentially as described by Vinogradov et al. (5). This apparatus is shown in Figure 1. It consists of three parts: reactor chamber; collection unit with trap T_1 and a storage bulb; and a part with trap T_2 and Hg manometer for the measurement of sulfur dioxide production. The collection unit is equipped with Pirani gauge for measuring pressure. The reactor chamber is a quartz tube with a sealed end which is attached to the collection unit by stainless steel union with a Teflon seal. This kind of union prevents the introduction of grease into the reactor interior. The trap T_3 protects the apparatus against penetration of oil vapors from the pump. A commercial porcelain boat is used as the reaction vessel. A piece of copper gauze (analytical grade) rolled up to form a plug serves as the deoxidation medium. Two electric furnaces are required in the procedure: (1) to heat the copper plug and (2) to heat the porcelain boat.

Reagent. Sodium metaphosphate, NaPO_3 , is prepared in a ceramic crucible by thermal decomposition of a commercially available NaH_2PO_4 which is then purified by melting and heating for 2 h at 900°C to remove organic and sulfur compounds (4). After cooling to room temperature chunks of NaPO_3 reagent are immediately crushed between sheets of Cu-foil by hammering. It is then stored in a desiccator.

Procedure. About 20 mg of BaSO_4 and 60 mg of NaPO_3 are weighed accurately and placed in a porcelain boat. The boat is inserted into the reactor as shown in Figure 1. The copper plug is then inserted into the tube and placed about 5 cm from the boat. After the reactor was connected to the collection unit, all stopcocks are opened and residual gases pumped away. When vacuum achieves about 10^{-3} Torr, stopcock C is closed and trap T_1 immersed in liquid nitrogen. At the same time, the temperature of furnace 2 is reset to 850°C which is reached in about 10 min. If the terminal temperature is acquired too fast, the reaction mixture may boil over!

After 25 min, stopcock D is closed and the furnaces are removed. Stopcock A is then opened, thereby allowing any noncondensable gases to be pumped away. After a short outgassing period, the sulfur dioxide is distilled from trap T_1 into trap T_2 , stopcock B

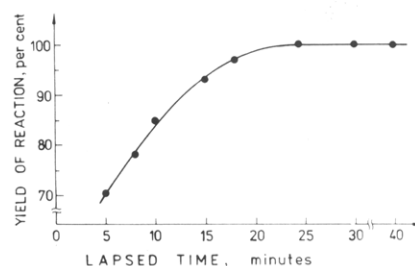


Figure 2. Reaction yield as a function of elapsed time. The yield is a percentage of the maximum possible by this method.

is closed, and the Dewar flask containing the liquid nitrogen is removed from trap T_2 .

When the SO_2 reaches room temperature its pressure is measured by a Hg manometer. The SO_2 is then transferred to a storage bulb or break seal by freezing. In routine analysis the pressure measurement is usually omitted.

After each series of six to ten runs, oxides that have accumulated on the copper gauze are reduced by hydrogen at about 700°C .

RESULTS AND DISCUSSION

Yield. Gravimetric and volumetric examination revealed that under the conditions described above, the extraction of sulfur dioxide is complete. The time needed for complete extraction was determined by observation of gas production over different stretches of time (Figure 2). At 850°C the reaction is sufficiently fast. Although increasing the reaction temperature accelerated the reaction itself, it is not advised because the NaPO_3 reagent rapidly evaporates at a higher temperature.

The reaction yields for strontium and calcium sulfates were tested manometrically, comparing the ratio of product pressures to the weight of substrates. When the reaction is complete these ratios should be inversely proportional to the molecular weight of sulfate, which indeed was the case.

Impurities in Sulfur Dioxide. Even in the most accurate gravimetric determinations of reaction yield, an excess in the order of 1% was detected. We have attempted to identify these impurities by a search of the mass spectra. The spectra of SO_2 samples (produced from BaSO_4 , CaSO_4 , and SrSO_4), standard, and background were scanned in the range of mass number from 10 to 70. Examination of these spectra led us to the conclusion that the major impurities in the sulfur dioxide produced are water and carbon dioxide.

Table I. $\delta^{34}\text{S}$ Measurements Against Laboratory Standard for International Standard Sample OGS-1 (BaSO_4), Which Were Obtained from Three Replicate Extractions

| extraction no. | results of analyses | av for individual extraction |
|----------------|---------------------|------------------------------|
| 1 | 20.15 | 20.06 |
| | 19.98 | |
| 2 | 20.11 | 20.12 |
| | 20.14 | |
| | 20.10 | |
| 3 | 20.14 | 20.16 |
| | 20.18 | |
| | 20.15 | |

Table II. Isotopic Analyses for SrSO_4

| specimen | $\delta^{34}\text{S}$ | av |
|--|-----------------------|-------|
| BaSO_4 from H_2SO_4 | 10.71 | 10.70 |
| | 10.63 | |
| | 10.71 | |
| | 10.74 | |
| SrSO_4 from H_2SO_4 | 10.47 | 10.63 |
| | 10.59 | |
| | 10.64 | |
| | 10.83 | |

The presence of CO_2 in sulfur dioxide may result from organic impurities and/or carbonates in the sulfate specimen. Natural samples should be treated by HCl and roasted to avoid these impurities. Treatment with HF is considered unnecessary inasmuch as silicates have no effect on the course of the reaction.

Some water in the produced sulfur dioxide is released from hygroscopic NaPO_3 when the reactor temperature is increased after degassing. Total elimination of chemically bound water (in NaH_2PO_4 molecules) seems to be impossible below melting point of NaPO_3 (610 °C). On the other hand, NaPO_3 degassing must be performed below this temperature as the production of SO_3 starts at a temperature only slightly above the melting point of the reagent. In order to decrease the amount of water in the prepared sample, we advise the following precautions: (i) the reagent should be rather coarse, (ii) it should be stored in a desiccator, and (iii) a large excess of the reagent should be avoided.

If natural sulfates contain a sulfide as well then obviously the sample should be purified to remove it prior to SO_2 extraction. By following the above precautions we obtain such a low level of CO_2 and H_2O that we have found a time-consuming procedure of sample purification to be unnecessary. However, in special cases, such purification can be performed in this apparatus by fractional sublimation at -131 °C (6) and trapping the water by dry ice-acetone mixture.

Isotopic Reproducibility. The isotopic reproducibility of the present method is comparable to the precision of our instrument which is 0.05 per mil. For illustration, $\delta^{34}\text{S}$ results obtained by replicate extractions of SO_2 from a BaSO_4 specimen are listed in Table I.

The preparation of sulfur dioxide from natural strontium and calcium sulfates under the conditions described above also lead to full yield of reaction and very good reproducibility. The isotopic compositions of SO_2 extracted from strontium and barium sulfates precipitated from the same sulfuric acid are shown in Table II. The average δ values obtained in this experiment are almost identical. Similarly, we have tested our method with respect to preparation of calcium sulfate. A sample of natural gypsum was dissolved in 10% HCl and barium sulfate was precipitated from the filtrate. Then both CaSO_4 and BaSO_4 specimens were roasted and analyzed by

Table III. Isotopic Analyses of CaSO_4

| specimen | $\delta^{34}\text{S}$ | av |
|--------------------------------------|-----------------------|-------|
| CaSO_4 | 21.87 | 21.97 |
| | 22.04 | |
| | 21.99 | |
| BaSO_4 from CaSO_4 | 21.73 | 21.94 |
| | 21.94 | |
| | 22.19 | |
| | 21.89 | |

duplicate SO_2 extractions. Table III presents the results of this experiment. Once again we obtained almost identical averages!

The Problem of Oxygen Correction. If the oxygen isotopic composition ($\delta^{18}\text{O}$) in SO_2 sample differs from those the SO_2 working standard, then the $\delta^{34}\text{S}$ value should be evaluated from (7)

$$\delta^{34}\text{S} = 1.0886\delta^{66} - 0.0886\delta^{18}\text{O} \quad (1)$$

for simple dual collector and

$$\delta^{34}\text{S} = 1.0929\delta^{66} - 0.0885\delta^{18}\text{O} \quad (2)$$

for Nier-type double collector. Two basic questions arise, therefore, concerning $\delta^{18}\text{O}$ in extracted SO_2 from sulfates of different oxygen isotopic composition: (i) Does $\delta^{18}\text{O}$ in SO_2 reflect the oxygen isotopic composition in prepared sulfate or rather in the reagent? (ii) How does one evaluate $\delta^{18}\text{O}$ in SO_2 ?

Our long-term experience gives the following answers to the above questions. In early experiments in which we used a small excess of NaPO_3 the SO_2 weakly reflected the $\delta^{18}\text{O}$ of the sulfates. This dependence, however, completely disappears with the addition of larger amount of NaPO_3 . The amount given above (60 mg of NaPO_3 /20 mg of BaSO_4) was found to be optimal. By use of such proportions for two specimens of BaSO_4 of identical sulfur isotopic composition, but differing in $\delta^{18}\text{O}$ by 52 per mil, only a small difference in δ^{66} of about 0.5 per mil was observed. Note that for this experiment one portion of H_2SO_4 was strongly enriched in ^{18}O prior to BaSO_4 precipitation with a small amount of heavy water. The natural variation range for $\delta^{18}\text{O}$ in sulfates only exceptionally exceeds 20 per mil. One may state, therefore, that even with natural variations of oxygen isotopic composition in sulfates, the SO_2 produced by this method has rather isotopically uniform oxygen due to "buffering" by the reagent.

The second question may be reduced to the following form: how to find a common additive correction for SO_2 produced from natural sulfates? This problem actually arises when we are going to express the result on the absolute CDT scale for a sulfate which will be used for years as a secondary sulfate standard. Soon the OGS-1 sample (BaSO_4 precipitated from ocean water) will be commonly used among other international standards distributed by NBS, Washington, and IAEA, Vienna. When such a sulfate is used, the additive term in eq 1 and 2 may be simply evaluated by the use of the appropriate equation for this standard $\delta^{34}\text{S}$. Absolute evaluation of $\delta^{34}\text{S}$ for OGS-1 standard was performed in our laboratory by using SO_2 produced in two ways: (i) by oxidation at 850 °C of silver sulfide with Cu_2O (8) and (ii) by extraction of sulfur dioxide from BaSO_4 using the method described in this paper. The BaSO_4 was produced from an Ag_2S sample by oxidation to SO_4^{2-} with HNO_3/HCl mixture. Details on the absolute evaluation of sulfur isotope standards will be published elsewhere (9).

CONCLUSION

The described method has been utilized in our laboratory for more than 2 years, and several thousand sulfate samples

were analyzed. Long-term reproducibility was achieved. This method has all the advantages of modified thermal decomposition method (3) and also some additional ones: (i) the temperature of reaction is significantly reduced; (ii) time consuming purification to remove CO₂ and H₂O may be omitted because of the high purity of SO₂; (iii) it can be used for all natural and precipitated sulfates and processing of these samples is performed under identical conditions; (iv) the same apparatus may be used for both sulfate and sulfide preparation; (v) its simplicity makes it suitable for the preparation of native sulfur and also, in some difficult cases, of sulfides converted into BaSO₄ as advised.

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Thermal Lens Calorimetry for Flowing Samples

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In order to utilize thermal lens calorimetry as a sensitive means of detection for liquid chromatography or automated analysis, we must consider the behavior of a thermal lens in a flowing sample. The major disturbance of the calorimetric response by the flow is caused by turbulent mixing in the illuminated region of the sample. At large flow rates, a loss of sensitivity, due to increased thermal conduction, and an additional source of proportional noise, from flow pulsations, are observed. The degradation of performance is not severe at flow velocities suitable for most applications.

The introduction of laser sources into spectrometric detectors for liquid chromatography (1-3) has produced significant gains in sensitivity and detection limits. The improvements over conventional sources arise not only from the increased intensity of the laser but also from the unique spatial coherence of the beam which facilitates focusing through small volume flow cells. The detection of LC samples having insignificant fluorescence quantum yields could be improved, similarly, by a calorimetric absorbance measurement using a laser source (4, 5). This idea was first proposed by Kreuzer (6) where the heat produced in the eluent by absorption of a pulsed CO₂ laser would be detected by a thermistor downstream from the laser beam; unfortunately, no details of performance were provided. In this work, the suitability of a related technique, thermal lens calorimetry, for detection of samples in a flowing stream is considered. The thermal lens effect, unlike other laser techniques, relies on the modification of the spatial coherence of the laser beam by the temperature distribution within the sample. It is important to consider, therefore, how the disturbance of the temperature profile by the flow will effect the thermal lens response.

In a thermal lens calorimeter, a lenslike element is formed within the sample by absorption of radiation from a TEM₀₀ laser beam, having a radially symmetric, Gaussian intensity distribution. The resulting temperature distribution, in the

case of a motionless sample, is governed primarily by radial thermal diffusion (7, 8). Following the onset of illumination by the laser beam, the temperature gradient approaches a steady-state condition where the rate of heating by the laser, which depends on laser power density and sample absorbance, equals the rate of heat loss, which depends on thermal conductivity and the temperature change produced. The time dependence of the focal length of the resulting lens has been derived (7)

$$f(t) = f(\infty)(1 + t_c/2t) \quad (1)$$

where $f(\infty)$, the steady-state focal length, is

$$f(\infty) = \pi k \omega^2 / 2.303 P (dn/dT) A \quad (2)$$

and t_c is the characteristic time constant given by

$$t_c = \omega^2 \rho C_p / 4k \quad (3)$$

where k is thermal conductivity in W cm⁻¹ K⁻¹, ω is the beam spot size in cm, P is the laser power in W, (dn/dT) is the variation in refractive index with temperature, A is the sample absorbance, ρ is the density, and C_p is the specific heat in J g⁻¹ K⁻¹. The thermal lens acts to change the divergence of the laser beam, which is detected as a change in the intensity of the beam center in the far-field, I_{bc} . When the sample is located one confocal length beyond a waist in the laser beam, the time dependence of I_{bc} is given by

$$I_{bc}(t) = I_{bc}(0) \left[1 + \frac{2.303EA}{1 + t_c/2t} + \frac{1}{2} \left(\frac{2.303EA}{1 + t_c/2t} \right)^2 \right]^{-1} \quad (4)$$

where E is the enhancement of the linear portion of the response compared to Beer's law (9), $E = -P(dn/dT)/\lambda k$. From the relative change in I_{bc} caused by the lens, an expression linear in absorbance may be obtained

$$(2\Delta I_{bc}/I_{bc}(\infty) + 1)^{1/2} - 1 = 2.303EA \quad (5)$$

A quantitative model of thermal lens behavior for a flowing sample is considerably more complex. A complete treatment