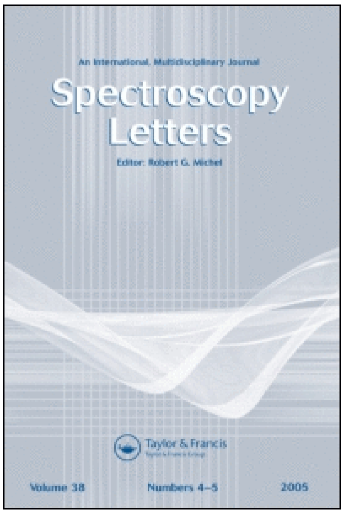

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THE MEASUREMENT OF THE SO_2 MOLECULAR ABSORPTION IN THE GRAPHITE FURNACE FOR THE POSSIBLE DETERMINATION OF SULFUR.

Key words: Sulfur dioxide molecular absorption: electrothermal vaporization, sulfur determination.

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ABSTRACT

The present study was conducted to investigate the molecular absorption of sulfur dioxide in a carbon rod furnace for the determination of sulfur. The arsenic atomic line at 206.98 nm emitted from an As- hollow cathode lamp was

used as an irradiation source in the measurements. The interferences caused by molecular absorption of some other molecules present in these conditions was also examined. Using the ionexchange as the pretreatment for the sample the method can be applied for a great variety of inorganic samples.

INTRODUCTION

Molecular absorption spectrometry has been developed for the determination of nonmetallic elements (Fuwa et.al.,Dittrich et.al.). These elements are difficult to determine by the conventional AAS methods because their resonance lines lie in the vacuum ultraviolet region. Molecular absorption of aluminium and indium monohalides formed at high temperatures have been used for the determination of halogens [1-3]. Sulfur has been determined as SO_2 by using special absorption cell consisting 1 cm x 273 cm Vycor tubing. Hydrogen disharge lamp has been used as the light source [4]. It has been shown that sulfur dioxide absorption spectra can be observed and sulfur can be quantified in flame where sulfur-containing solution is introduced. The molecular sulfur dioxide has in the ultraviolet absorption spectrum four band systems between 320.0 - 260.9 nm, 230.0 - 180.0 nm, 158 -152 nm and below 135.0 nm [5].The strong absorption band at 207 nm has been used for the determinations in flame by method described above.

The development of a simple, sensitive and precise method for the determination of this element would provide a much needed analytical tool. For this reason the possibility, that the measurement of sulfur can be accomplished by SO_2 absorption in a carbon rod furnace has been explored. The use of atomic lines of various elements was studied for the measurement of the absorption. For the measurements the line at 207 nm was chosen because the strongest absorption band lies at this wavelenght.

EXPERIMENTAL

Apparatus

The molecular absorption of sulfur dioxide was measured with a Pye Unicam SP 9-800 Spectrometer equipped with a deuterium lamp background correction system for the simultaneous background correction. Measurements were carried out using ordinary uncoated graphite furnaces. Nitrogen gas was used to purge the air from the furnace. Molybdenum, arsenic, silver and nickel Cathodeon Ltd hollow cathode lamps were tested for the use as irradiation sources. The H_2S absorption measurements were carried out using an arsenic Cathodeon Ltd hollow cathode lamp. The spectral bandwidth of the monochromator was 0.2 or 0.5 nm.

Procedure

The experimental conditions for the final measurements of sulfur dioxide molecular absorption are given in Table 1. In practical measurements the ion exchance is needed in the case of the real samples in order to remove the interfering cations. In the Table 2 are presented the experimental conditions for the measurement of possible absorption of hydrogen sulfide.

TABLE 1.

Experimental conditions for SO_2 molecular absorption measurements.

Injection of sample	10 µl	
(Injection of nitric acid	10 µl)	
Preconsentrating	110 C	5 s.
Consentrating/drying	130 C	10 s.
Evaporation and measurement	1600 C	7 s.

TABLE 2.

Experimental conditions for H_2S molecular absorption measurements

Injection of sample	10 uL	
Preconsentrating	110 C	5 s.
Consentrating/drying	130 C	10 s.
Evaporation and measurement	200-700 C	7 s.

Chemicals

All the reagents used were pro analysis grade of Merck. The ion exchange resin was Ambelite IR 120. All solutions were prepared using deionized and distilled water.

RESULTS AND DISCUSSION

The sulfur dioxide has a strong molecular absorption spectrum between 200- 220 nm [4]. The maximum of this absorption lies at 207 nm. This wavelength was choosen for the measurements of sulfur dioxide molecular absorption using a sharp line irradiation source. In order to find a suitable sharpline irradiation source, hollow cathode lamps, those have emission lines near 207 nm were selected with the help of the MIT wavelength tables [6]. Arsenic, molybdenum, silver and nickel seemed to have suitable lines and the hollow cathode lamps of these elements were chosen for the investigations. The test of the lamps was excequted by measuring the SO_2 absorptions using standard solutions containing 100 and 1000 mg/L of sulfate. The best results were obtained by the atomic line of arsenic at 206.98 nm. Because the line widths of the atomic lines emitted from a hollow cathode lamp are very narrow (ca. 0.001 nm) the sensitivity of the analysis in atomic absorption spectrometry using a sharp line irradiation source should not depend on the slit width of the monochromator provided that different atomic lines can be separated fron each other. It can be expected that the slit width has only a minor or no effect on the intensity of SO_2 molecular absorption if a hollow cathode lamp having only

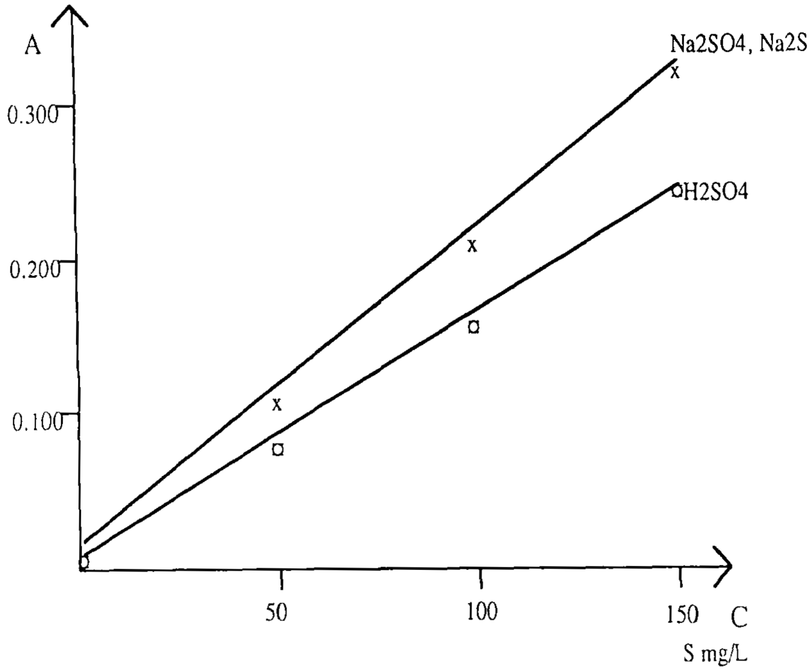

FIG. 1.The calibration graphs got by using the different sulfur solutions. The calibration graph obtained by using potassium sulfate was the same as with the sodium sulfate.

one emission line at the SO_2 absorption band is used. This has been found to be true when the SO_2 absorption was measured with the arsenic hollow cathode lamp using slitwidths 0.2 and 0.5 nm.

The calibration graphs measured using arsenic lamp are presented in Fig 1. The standard solutions were preparedfrom H_2SO_4, Na_2SO_4 and Na_2S. The amount of sulfur can be determined from some metal compounds using

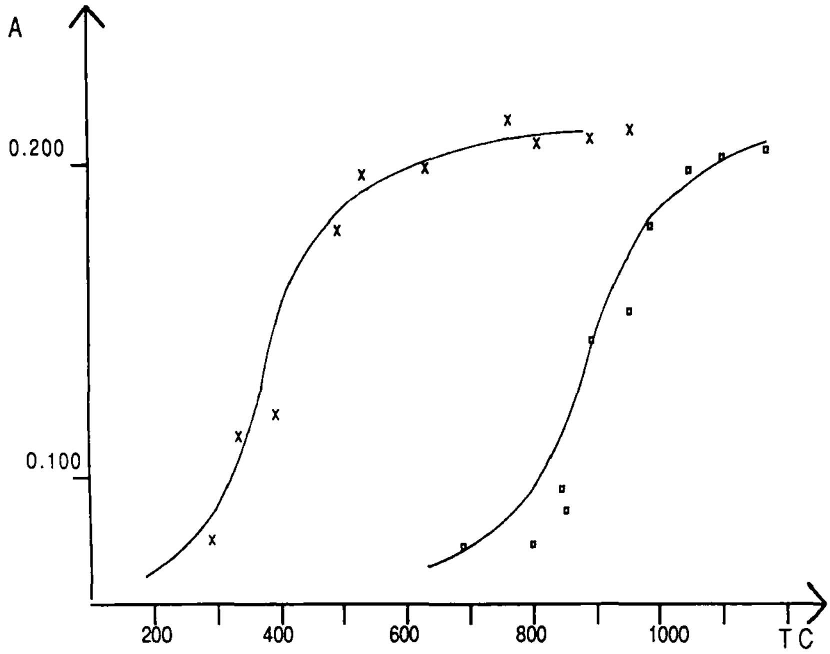

FIG. 2. The formation of sulfur dioxide from sodium sulfide (x) and sodium sulfate (□) in different temperatures.

calibration graph obtained by sodiun sulphate or sodiun sulfide standards. The calibration graph obtained by potasium sulpate standards is the same as that of sodium sulfates. The absorptions measured using sulphuric acid solutions are slightly weakier than absorptions measured by salt standards. This is due to the easier evaporation of sulphur dioxide before the measurement step when sulfuric acid is used as the standard, because in the furnac exist no metals to bind the sulfate. The formation of sulfur dioxide from sodium sulfide and sodium sulfate was studied in different temperatures. Fig. 2 shows that from the sodium sulfide the formation of sulfur dioxide begins at much lower temperatures than that from the sodium sulfate. It can be concluded, that using this furnace temperature program there is oxygen enough in the furnace to react with sulfur to form solfur dioxide even when sulfur is injected as the sulfide form. Finally, the absorption and the amount of sulfur dioxide at higher temperatures is the same from both of these compounds.

Molecular absorption of some other compounds

Hydrogen sulfide has a quite strong absorption near the absorption of sulfur dioxide and the maximum of this absorption lies between 190 -200nm [7]. In order to evaluate the possible interference caused by the possible formation and absorption of H_2S when the measurements are performed at the maximum of this absorption. Measurements of hydrogen sulfide were carried out at 193.7 nm using an arsenic hollow cathode lamp without background correction. The measurements done at this wavelenght showed that at the temperatures of sulfur dioxide measurements in the furnace is no interfering amounts of hydrogen sulfide. At lower temperatures, between 200 and 600 nm it was, however, possible to measure weak absorbances at this wawelenght (Fig 3.). Many alkali halides have strong absorption spectra near the same area as sulfur dioxide. From these , especially the absorption spectra of sodium chloride, bromide and iodide and potassium chloride, bromide and iodide have been observed and identified [9]. The absorption maxima of these spectra lie at lower wavelengths than the SO_2 absorption, but some absorption has been measured at the same wavelength with the SO_2 absorption. In order to investigate the

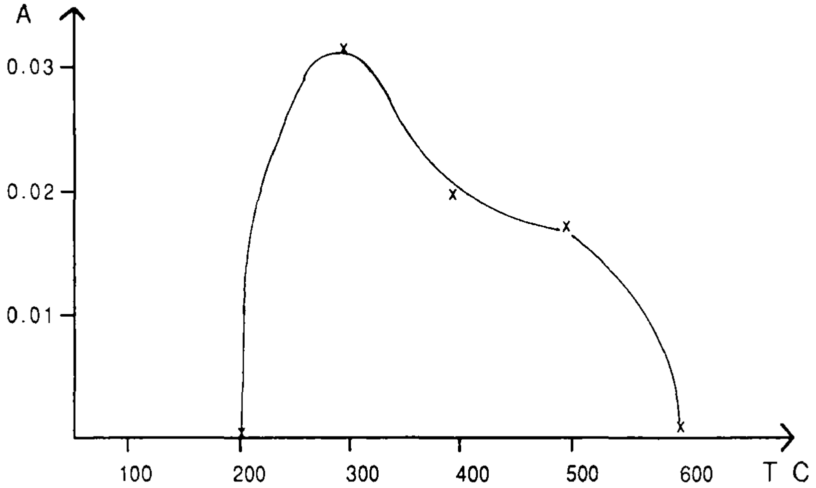

FIG. 3. Absorptions in different temperatures measured at 193.7 ,where hydrogen sulfide has strong absorption.

interferences caused by those compounds, absorption measurements using solutions having different consentrations of these compounds in distilled water were carried out. Comparison between these measurements and those obtained with solutions containing 50 mg/L of sulfur are presented in Table 3. The absorptions caused by sodium bromide and iodide, and potassium bromide and iodide are high, whereas the absorptions caused by sodium and potassium chlorides are much lower.

Interferences

Alkali halides are causing serious interferences when their consentrations are higher than 5 - 10 mg/L. The other type of interferences would obviously

TABLE 3.

Consentrations of alkalihalide molecules causing the same absorbance as 50 mg/L of sulfur (SO_2) in the same conditions as sulfur dioxide was measured.

Molecule	Consentration mg/L
NaCl	370
NaBr	110
NaI	130
KCl	470
KBr	150
KI	160

be caused by the formation of metal sulfides formed at high temperatures [6]. The ion exchange is the easiest procedure to avoid both of these types of interferences. The interferences caused by different acids was investigated by measuring sulfur in nitric and hydrochloric acid solutions. The hydroloric acid did not have any effect on the formation and absorption of SO_2. When the consentration of nitric acid was higher than 0.02 M, the formation of SO_2 became more effective and the absorption began to increase. If the measurements has to be performed in solutions having 0.02 M or more nitric

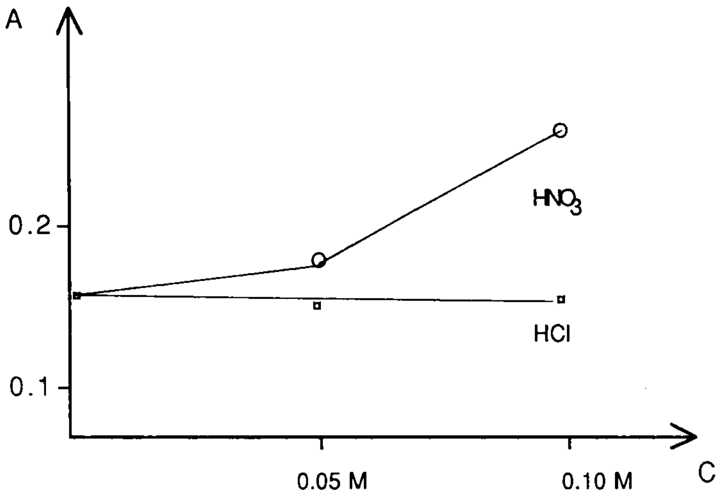

FIG. 4. The effect of the increasing nitric and hydrochloric acid consentrations in the sample solution on the absorption of SO_2.

acid the interference can be avoided by using 0.2 M nitric acid as a matrix modifier. In addition, this will increase the sencitivity of the method from 5 to 3 mg/l. In any case, the interferences caused by HCl and HNO_3 on SO_2 absorption are not serious at low acid consentrations (Fig 4.). For example, if the sample contains nitrate less than 600 mg/L, after the ion exchange nitric acid will cause no interference.

CONCLUSIONS

The proposed method utilizing molecular absorption of SO_2 afford an easy method for the determination of sulfur. The sample preparation is relative rapid

TABLE 4.

Analytical data of SO_2 molecular absorption measurements.

Characteristic consentrations (1% -absorption)	5 - 3 mg/L
Dynamic range	up to ca. 300 mg/L
Precision (RSD)	7%

and simple, only dissolution and ion exchange are needed. The absorption of some alkali halides and formation of stable metal sulfides may cause interference in some cases if the ion exchange is not performed. The precision and accuracy of the method are also good. The analytical data is given in Table 4. Sulfur can be determined in some organic compounds without any sample pre-treatment and using the ion exchange the method can be applied to a great variety of inorganic samples and no special equipments or skills are required.

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