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TRACE ANALYSIS OF CERTAIN CATIONS AND ANIONS: SULFUR SPECIES
IN SOLIDS AND COPPER(I) IN AQUEOUS SOLUTIONS

The University of Arizona

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TRACE ANALYSIS OF CERTAIN CATIONS AND ANIONS:
SULFUR SPECIES IN SOLIDS AND COPPER(I)
IN AQUEOUS SOLUTIONS

Prepared by
Jau-Hwan Tzeng

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMISTRY
In Partial Fulfillment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

1983

THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read
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entitled Trace Analysis of Certain Cations and Anions:
Sulfur Species in Solids and Copper(I) in Aqueous
Solutions

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ABSTRACT

A nitrogen-cooled and an argon-cooled hydrogen flame have been used for the determination of sulfur containing species in solids by molecular emission cavity analysis (MECA). The argon-cooled flame is much more sensitive for the determination of SO_4^{2-} . In a solid mixture containing S_8 , S^{2-} , SO_3^{2-} , and SO_4^{2-} , the presence of one or more of these sulfur containing species can be determined with the argon-cooled flame. The nitrogen-cooled flame can be useful, for example, in the determination of a mixture of S_8 and SO_3^{2-} in a solid matrix. All these sulfur containing species can be quantitatively determined in the argon-cooled flame in the concentration range from about 10 ppm to 5000 ppm. The variation from 10 percent to 30 percent in the reproducibility of these measurements has been attributed to the non-homogeneity of the solid materials and the small sizes required.

Sulfur dioxide has been used for the reduction of ammoniacal copper(II) solutions to solutions containing various copper (I) compounds. These copper(I) compounds can be reduced further to copper metal by varying the solution conditions. The mechanisms of the reactions involved must be understood before they can be successfully used for the large scale production of copper. Porth et al.'s method was followed for the synthesis of Cu(I) intermediates. Several compounds were isolated and their compositions determined. The changes

in the relative concentrations of Cu(I) and Cu(II) are also important for unraveling the kinetics and mechanisms of these reactions. A simple spectrophotometric method using 2,9-dimethyl-1,10-phenanthroline was developed to monitor the Cu(I) concentration in solution. The sensitivity of the method is sufficient to determine 10^{-5} M Cu(I) in the presence of Cu(II); SO_2 , however, interferes with the method. Other possible methods including the use of a mixture of EDTA and 2,9-dimethyl-1,10-phenanthroline were also examined. Evidence is presented for the formation of a ternary complex of copper(I), 2,9-dimethyl-1,10-phenanthroline, and EDTA. The possibility of using a mixture of Cu(II) and 2,9-dimethyl-1,10-phenanthroline to determine SO_2 was tested. Oxygen was found to interfere with this method.

CHAPTER 1

DETERMINATION OF SULFUR SPECIES BY MOLECULAR EMISSION CAVITY ANALYSIS

Introduction

If an aerosol of a sulfur compound is introduced into a fuel-rich hydrogen flame that has a relatively low temperature, an intense blue emission from S_2 is observed and the blue emission is enhanced at a cold surface placed in the flame. This phenomenon was first observed by Salet (1) and has been known as the Salet phenomenon. In 1931, Fowler and Vaidya (2) described the S_2 emission that was observed in the flame emission of carbon disulfide. Crider (3) rediscovered the Salet phenomenon and developed a sensitive detector for monitoring sulfur dioxide and sulfuric acid in air samples. Dagnall et al. (4) investigated the determination of sulfur compounds by measurement of the S_2 emission from these compounds when they were introduced as aerosol solutions into a hydrogen flame diluted with nitrogen and argon. Park and Veillon (5) also used the Salet phenomenon to determine sulfur compounds in aqueous and organic samples.

MECA is an acronym for molecular emission cavity analysis. This technique employs a small cavity at the end of a rod into which the samples are deposited. The cavity is introduced into the nitrogen-hydrogen-air flame and the resulting emission is recorded. This technique was first developed by Belcher et al. (6) and has been used to

determine both metals and non-metals (7). The important features of this technique are the relatively cool flame that is necessary to observe the molecular emission and the specially designed cavity that accommodates the sample.

The cool flame gives rise to molecular emission and obviates the need for hotter excitation sources. A high resolution monochromator is not required because a relatively broad band molecular emission between 200 and 500 nm is monitored. The flame itself produces little emission in the visible and UV regions. The background emissions arise only from the OH band which emits at 306 nm and a very weak continuum covering the visible region. This lack of background flame emission allows the relatively weak molecular emission from added species to be detected.

If a sample solution is aspirated into a cool flame, an excessive number of desolvated solid particles may remain intact and thereby reduce the number of molecular entities in the gas phase. As a consequence, the precision as well as the sensitivity of the method are affected. The advantage of the MECA cavity is that the sample can be introduced in a reproducible manner into a specific region of the flame and the sample will remain in the cavity until a sufficiently high temperature is reached, when vaporization occurs. An additional advantage is that only small sample amounts are needed and solids (mg), as well as liquids (μL) can be used.

The Salet phenomenon is utilized in MECA because the cavity serves as a cold surface. This effect was demonstrated by Belcher and coworkers (6) and confirmed by Calokerinos (7), who measured the effect of cavity cooling on the emission intensities by introducing a constant

flow of various vapors into the MECA cavity situated in a hydrogen based flame. The S_2 emission from carbon disulfide was found to gradually increase as the cavity temperature decreased.

In the flame, the cavity temperature gradually increases. When the cavity containing sample enters the flame, several processes occur: 1) solvent evaporation, 2) analyte vaporization, possibly as a result of decomposition, 3) formation of emitting species from analyte vapor, 4) excitation, and 5) emission and quenching. The vaporization processes are measured in seconds and are much slower than the other steps. Based on this, time resolved results were obtained by Belcher et al. (8,9). They used MECA to determine certain sulfur anions simultaneously in an aqueous solution.

A method based on MECA was proposed for the determination of S^{2-} , S_8 , SO_3^{2-} , and SO_4^{2-} in solids (10,11). In this method, a solid sample containing one or more of these sulfur containing species was weighed in a small aluminum cup which was placed in a quartz-lined cavity that was fitted on the end of a stainless steel rod. A solution containing phosphoric acid and a wetting agent was added to the solid sample and the end of the steel rod was positioned in a relatively cool hydrogen-nitrogen flame. The emission from the molecular sulfur that was produced in the cavity was recorded at 384 nm as a function of time. The peaks in the emission spectrum were identified with each of the sulfur containing species in the solid sample, and the peak areas or peak heights were used in conjunction with a calibration curve to determine the concentration of each of the sulfur species.

In this method, it is evident that there are several variables that must be carefully controlled to obtain the maximum sensitivity and an acceptable reproducibility. The sensitivity of the method is governed by the intensity of the flame emission, which depends on the population of the molecular sulfur species, S_2 , in the excited state, and their residence time in the flame. Although the mechanism of formation of molecular sulfur from the various sulfur containing species is not fully understood, it has been established that several characteristics of the flame, in particular its temperature, affect the emission intensity. The excited state S_2 molecules that emit are almost exclusively produced by radical interactions rather than by thermal excitation. If monoatomic argon gas is substituted for the diatomic nitrogen gas in the MECA flame, the number of radicals quenched by collisional processes in the flame should decrease. As a consequence, the number of S_2 molecules in the excited state should also increase. We have observed that, under comparable conditions, the emission intensity of S_2 molecules produced in a hydrogen-argon flame is greater than that in a hydrogen-nitrogen flame. In this work we have compared the use of these two types of flames in the determination of sulfur containing compounds by MECA.

Additional variables that affect the emission intensity are the concentrations of the components of the wetting solution (H_3PO_4 and Triton X-100), and the surface composition of the material that was used in the fabrication of the sample cup. In all our previous work that was reported (10,11), small aluminum foil cups, 3 mm in diameter and 2 mm deep, were used and no special attention was paid to the nature of the

aluminum surface. In subsequent experiments, however, we have observed that the emission intensity produced in the cavity is dependent on the previous history of the aluminum foil surface.

In the work that is reported below, we have adopted an empirical approach in our attempts to maximize the signal: noise ratio and to separate the emission peaks that are obtained from solid samples containing sulfur in several oxidation states. The effects of all the variables mentioned above have been studied and an optimum set of operating conditions has been found for the identification and determination of sulfur containing molecules and anions in a solid matrix. Attempts were made to use the MECA technique for the determination of sulfur containing species in coal and other sulfur containing solids.

Experimental

Instrumentation

The MECA apparatus is a regular flame emission system with a modified burner and a sample introduction device as shown in Figure 1.1. The flow rates of different gases from gas cylinders are controlled by the regulators and flow meters (Matheson, Model 602 for hydrogen and Model 603 for nitrogen, argon and air). The gases are mixed and passed through the burner (Figure 1.2) which is fitted with a Teflon flashback plug.

The aluminum sample introduction device (Figure 1.2) contains several parts:

- A. Rotating turret: upright position for sample loading and horizontal position for sample introduction.

- B. Sample arm, made of stainless steel.
- C. Cooling coil; water cooled coil of 3 mm (o.d.) copper tubing.
- D. Sample cavity, 6 mm i.d. and 5 mm deep at the end of the sample arm.
- E. Neoprene O-ring, in order to hold the cooling coil.
- F. Fixed stop to position the rotating arm of the sampling device at an angle 7° below the horizontal.

The details of the MECA cavity are shown in Figure 1.3. Four lateral slits (A) are equally spaced around the circumference of the sample cavity to allow for thermal expansion and to hold the quartz cup (B), 6 mm (o.d.) and 4 mm deep. The aluminum sample cup (C) which is 3 mm in diameter and 2 mm deep is placed in the quartz cup.

The intensity of the emission signal at a fixed wavelength is measured with the aid of a monochromator (GCA/McPherson model EU-700-2) and a photomultiplier detector (GCA/McPherson model EU-701-30). The current in its detector circuit is converted to voltage by a Keithley model 480 picoammeter and recorded on a Linear model 252A integrating chart recorder interfaced through a General Radio type 1432-J decade resistor to expand the input voltage ranges.

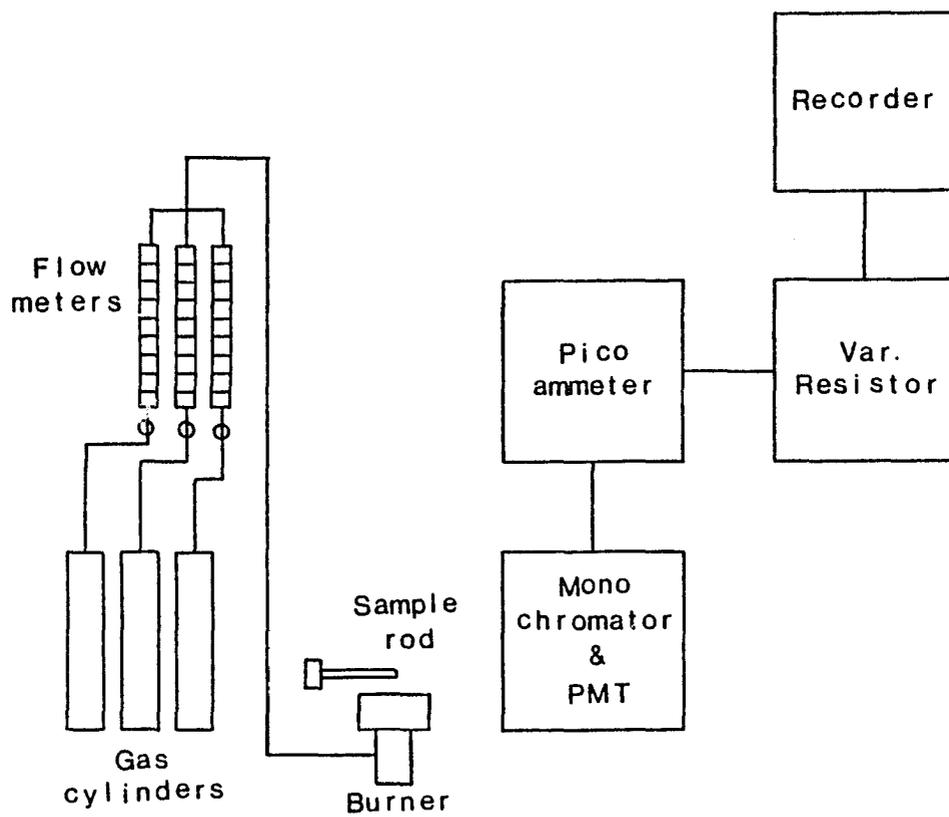


Figure 1.1. The MECA apparatus.

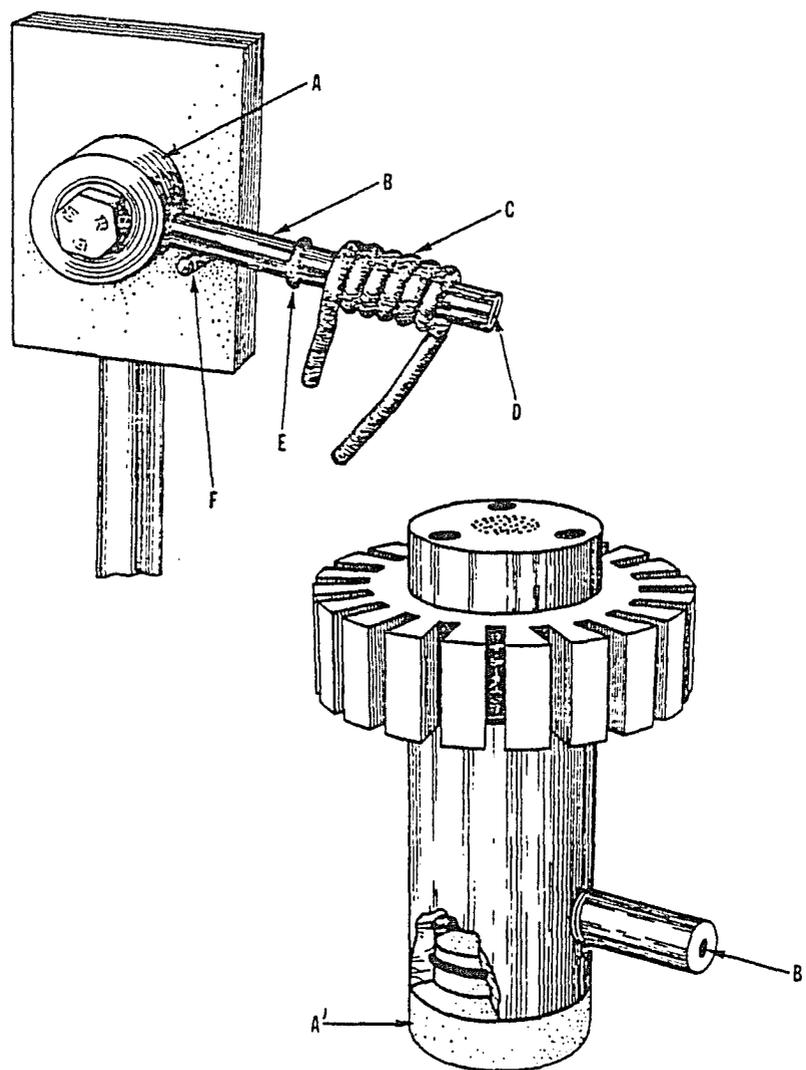


Figure 1.2. Expanded view of burner and sample introduction device--A' Teflon flashback plug, B' gas inlet. (A) Rotating turret, (B) sampling arm, (C) copper cooling coil, (D) sample cavity, (E) neoprene O-ring, (F) fixed stop.

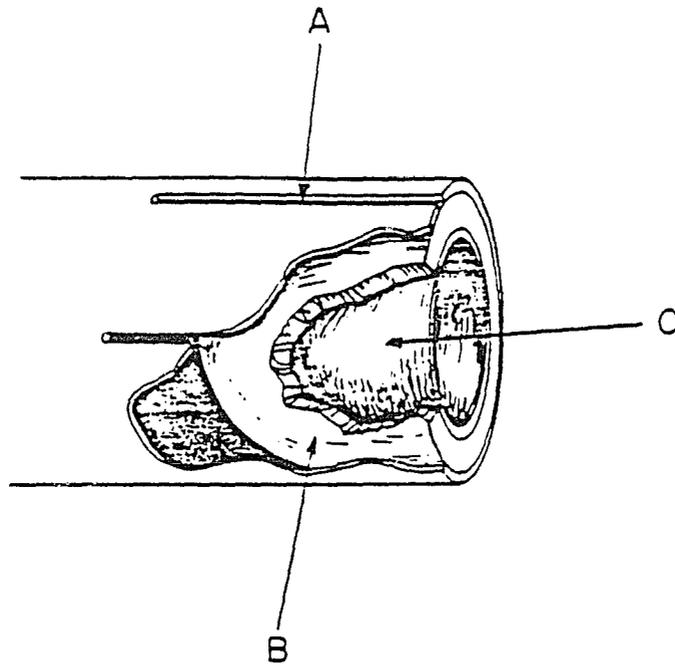


Figure 1.3. Cutaway view of stainless steel sample cavity--A) expansion slit, B) quartz cup, C) aluminum sample cup.

Reagents

Gas: Argon, hydrogen, air, and nitrogen used without further purification.

Solutions: Phosphoric acid and sulfuric acid diluted from concentrated reagent grade acid solutions. Triton X-100 is a polyethylene glycol ether of monoisooctylphenol manufactured by Rohm and Haas Company. It is a surfactant and is used to hasten wetting of the samples by decreasing surface tension.

About 13 μL of a mixture of H_3PO_4 and Triton X-100 (13 $\mu\text{L}/100$ mL of 0.075 M H_3PO_4) are used as wetting solution for general MECA analysis.

Solids: Solid standards containing one or more sulfur species were prepared from analytical reagent grade chemicals: elemental sulfur as sublimed sulfur (S_8), sulfite as sodium sulfite, sulfate as sodium sulfate, sulfide as copper sulfide (Ultrapure 99.998 percent) or lead sulfide (Ultrapure 99.999+ percent). A range of concentration of the solid sulfur containing species was obtained by diluting with silicon dioxide (325 mesh), and 99.9 percent pure from Alfa Chemicals by the following process:

1. All solid components are reduced to 325 mesh. Solid samples are ground with a mortar and pestle and then sifted through a 325 mesh sieve. The Spex Industries model 3536 nylon sieve set was used.
2. Mix about 1:1 solid sample and silicon dioxide and place in a polystyrene vial weighed to the nearest 0.01 mg. The vial (0.5" in diameter and 2" long) also contains five plexiglass

balls (0.125" in diameter) for mixing purposes. The total volume of the solid sample and silicon dioxide should not exceed one third of the vial volume.

3. The constituents in the vial are mixed in a model 3110-3A Wig-L-Bug with a model 3113 adapter for 10 minutes (the Wig-L-Bug, polystyrene vials, and plexiglass balls were obtained from the Crescent Dental Manufacturing Co., Lyons, IL).
4. Less concentrated standards are obtained by repeating the dilution as described in steps 2 and 3.
5. Mixtures of several sulfur species are obtained by mixing the diluted single component sample followed by steps 2 and 3.

Aluminum Sample Cup

A small disposable aluminum cup is used for weighing and handling solid samples. This cup is made as follows:

1. Use a paper punch to punch aluminum foil (0.025 mm thick) and obtain 6 mm diameter discs.
2. Spread the aluminum discs on a sheet of rigid styrofoam.
3. Place a 3 mm diameter and 12 cm long metal rod on the center of a single disc and positioned perpendicularly to the surface of the disc.
4. Push the rod downward. The outer portions of the disc mold around the tip of the rod.
5. Pass the rod with the partially formed aluminum cup through a 3.5 mm i.d. piece of tubing. A cup is formed.
6. Check the cup. Only use cups that are not damaged.

Cavity Position

The cavity position was optimized by Schubert in the following manner (12). First, the cavity opening is aligned with the entrance slit. Then, the burner is positioned as close as possible to the monochromator and just below the entrance slit, care being taken not to expose the monochromator to heat from the flame. Next, the cavity is moved horizontally toward the monochromator and into the flame until a maximum response is obtained with a diluted sulfite solution. At this point, the sample introduction device is secured and the burner is moved vertically downward until the response is again maximal with the sulfite solution. After the burner was secured and the flame extinguished, the center of the cavity was found to be in the flame at a distance of 4 mm from the edge of the flame and the bottom of the cavity was 12 mm above the burner head.

Analytical Methodology

Analysis Procedure

- a. Warm the sample cavity and check to determine whether the cavity is contaminated by placing the sampling arm in the flame. In this way, the baseline is obtained.
- b. Remove the empty cavity from the flame. The time interval between sample runs is usually not sufficient for the cavity to cool completely to room temperature. These first two steps permit the cavity to stabilize at its normal, somewhat elevated, pre-introduction temperature. Thus, the first sample will begin at the same temperature as succeeding samples.

- c. Add wetting solution to the sample weighed in a small aluminum cup.
- d. Place the aluminum cup in the sample introduction device by using a pair of tweezers.
- e. Place the sample in the flame by rotating the sample rod.
- f. Record the emission intensity.
- g. Remove the sample from the flame by rotating sample rod to its original upright position.
- h. Remove the sample cup.

Emission Spectrum of Molecular Sulfur

When sulfur or its compounds undergo combustion, the flame emission spectra consists of emission bands that can be attributed to S_2 , SO , SH , and CS superimposed on a background continuum. The intensities of the different emission bands are dependent on the nature of the flame. All these emission bands have been discussed by Gilbert (13). The S_2 emission band has been chosen for most spectrochemical analysis. For example, Dagnall et al. (4) described the measurement of the S_2 band emission at 384 nm in a nitrogen-diluted hydrogen diffusion flame and in a pre-mixed air-hydrogen flame burning inside a cooled sheath. In a nitrogen-diluted hydrogen flame, inorganic and organic sulfur compounds also give the characteristic blue S_2 emission in the MECA cavity (7)

When the $Ar/H_2/air$ flame was used in this laboratory, each of the compounds, Na_2SO_4 , Na_2SO_3 , S_8 , CuS with added wetting solution gave emission spectra that were recorded in the wavelength range 340 nm to 440 nm. All compounds showed the S_2 emission band in

the Ar/H₂/air flame. The emission spectrum of Na₂SO₄, obtained under these conditions is shown in Figure 1.4. The S₂ emission was monitored at 384 nm in all subsequent work.

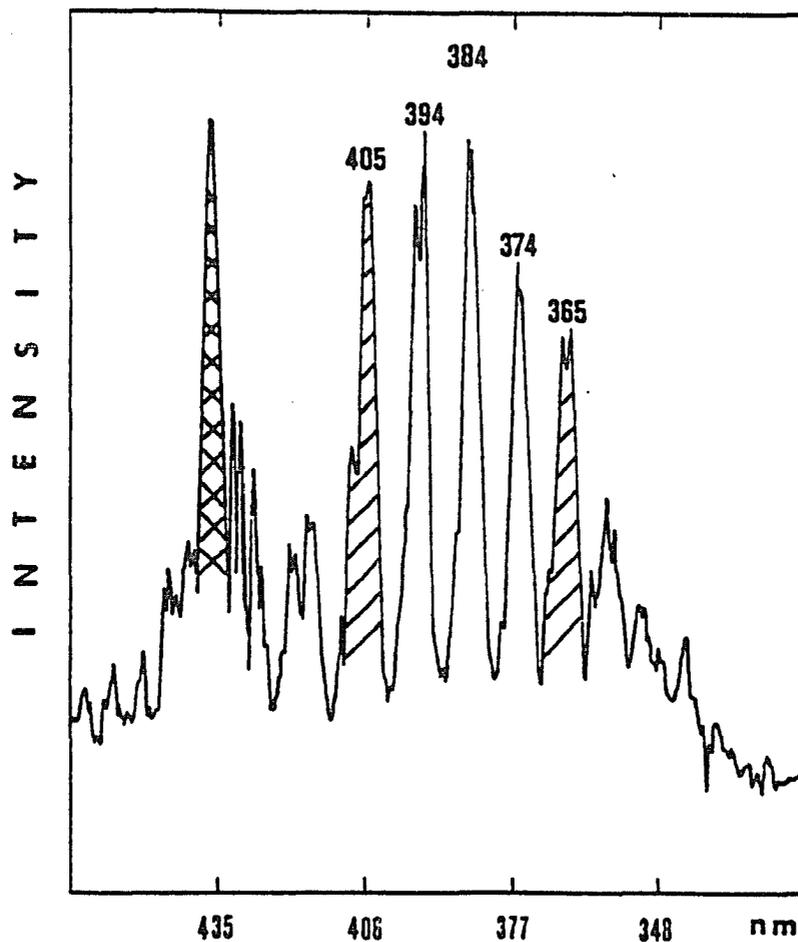


Figure 1.4. Emission spectrum of S_2 in the $H_2/Ar/air$ flame. The intense band at 437 nm which is crosshatched arises from the external illumination in the laboratory. The S_2 emission and the external illumination contribute to the diagonally shaded bands at 405 and 365 nm. The S_2 emission spectrum was produced by pure Na_2SO_4 at a scan rate of 20 Å/s. The full width at half-maximum of the peak at 384 nm was 4 nm.

The Time Dependent Formation of Molecular Sulfur From Various Sulfur Species

Belcher et al. (6) have studied the S_2 emissions that were produced by aqueous solutions of various sulfates, e.g., H_2SO_4 , $FeSO_4$, $MnSO_4$, Na_2SO_4 with the N_2/H_2 /entrained air flame. They found that the time (t_m), taken for a given sulfate compound to reach its maximum emission intensity is characteristic of that compound and is related to the thermal breakdown and volatilization which occurs in the presence of the flame gases. They attempted to measure the cavity temperature by inserting a chrome-alumel thermocouple into the cavity via a hole drilled from the side of the cavity and determined the temperature at which each compound reached a maximum peak intensity. The results are shown in Table 1.1.

Some results show that even below the decomposition temperature of compounds, the S_2 signal is observed. Belcher and co-workers indicated that free radicals in the hydrogen flame may help to produce the S_2 emission at temperatures lower than the decomposition temperature.

Table 1.1. Decomposition temperature of different sulfate compounds.

<u>COMPOUND</u>	<u>APPROXIMATE TEMPERATURE (°C) MEASURED</u>	<u>REPORTED DECOMPOSITION TEMPERATURE (°C)</u>
H ₂ SO ₄	350	330 (b.p.)
FeSO ₄	550	>720 (decomp.)
CoSO ₄ · 7 H ₂ O	530	830 (decomp.)
MnSO ₄ · 4 H ₂ O	640	>940
Na ₂ SO ₄	820	>880

Later, Belcher et al. found that H_3PO_4 can be used to release H_2SO_4 from aqueous solutions of sulfate compound (14). After adding H_3PO_4 to different aqueous sulfate solutions, the sulfate compounds as well as H_2SO_4 , gave the same t_m value. After adding H_3PO_4 the t_m value for $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 decreased slightly and the signal intensity was enhanced. These workers speculated that these results may be caused by changes in thermal conductivity and that the phosphoric acid coating may have reduced the rate of hydrogen atom recombination. In 1976, Al-Abachi et al. (9) successfully determined certain sulfur anions in admixture. For example, mixtures containing $\text{SO}_3^{2-}-\text{SCN}^- -\text{SO}_4^{2-}$, and $\text{S}^{2-}-\text{SO}_3^{2-}-\text{SO}_4^{2-}$ were determined. Schubert et al. first determined S_8 , SO_3^{2-} , SO_4^{2-} and S^{2-} in solid samples (11) in the N_2/H_2 /entrained air flame; the time resolved results are shown in Figure 1.5. I have tried to determine sulfur species in both Ar/H_2 /air flame and the nitrogen/ H_2 /entrained air flame. The values of t_m , the time at which the characteristic S_2 emission maximum appeared in the cavity when positioned in H_2/Ar /air flame, were recorded for sulfide, elemental sulfur, sulfite, and sulfate. If H_3PO_4 was not added to the solid sample, sodium sulfite and elemental sulfur, S_8 , gave emission peaks with the same t_m value (2s). Copper(II) sulfide and lead sulfide gave two peaks, a very weak peak at $t_m = 2\text{s}$ and a very strong peak at $t_m > 30\text{s}$, but no peak was observed for sodium sulfate. The results were quite different when the emission spectra were recorded after the addition of H_3PO_4 solution to the solid samples; sodium sulfite gave three peaks, a very strong peak at $t_m = 4\text{s}$ and two weak peaks at $t_m = 12$ and 17s ; elemental sulfur

gave one peak at $t_m = 12s$; copper(II) sulfide or lead sulfide gave two peaks, a moderately strong peak at $t_m \sim 12s$ and a very strong peak at $t_m > 40s$; sodium sulfate gave a single strong emission peak at $t_m = 17s$. The relative intensities of the peaks in the emission spectra of sulfur-containing solids in the Ar/H₂/air flame in the presence of the H₃PO₄ solution and in the absence of H₃PO₄ solution are shown in Figure 1.6. In the N₂/H₂/entrained air flame the S₂ emission peak from SO₃²⁻ appears first ($t_m < 5s$) and is followed by the peaks from S²⁻ and S₈ which are difficult to resolve ($20s < t_m < 27s$); the emission peak from SO₄²⁻ appears at $t_m > 35s$. All these results are collected in Table 1.2.

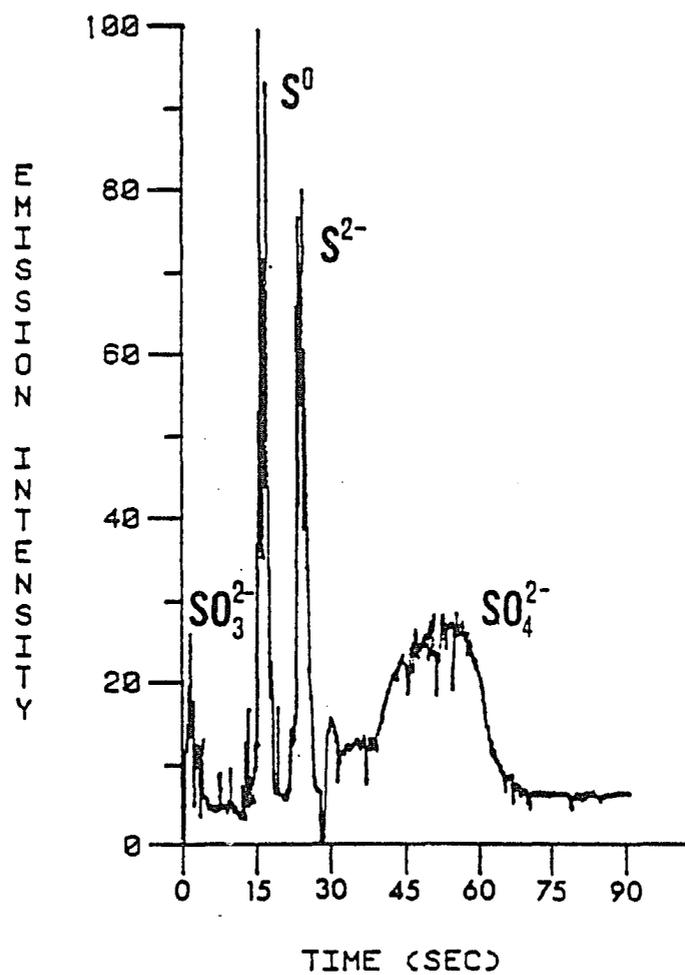


Figure 1.5. Characteristic emission responses of four inorganic forms of sulfur as a function of time--relative sulfur concentrations due to sulfite, elemental sulfur, sulfide, and sulfate are approximately 1:1:8:9, respectively.

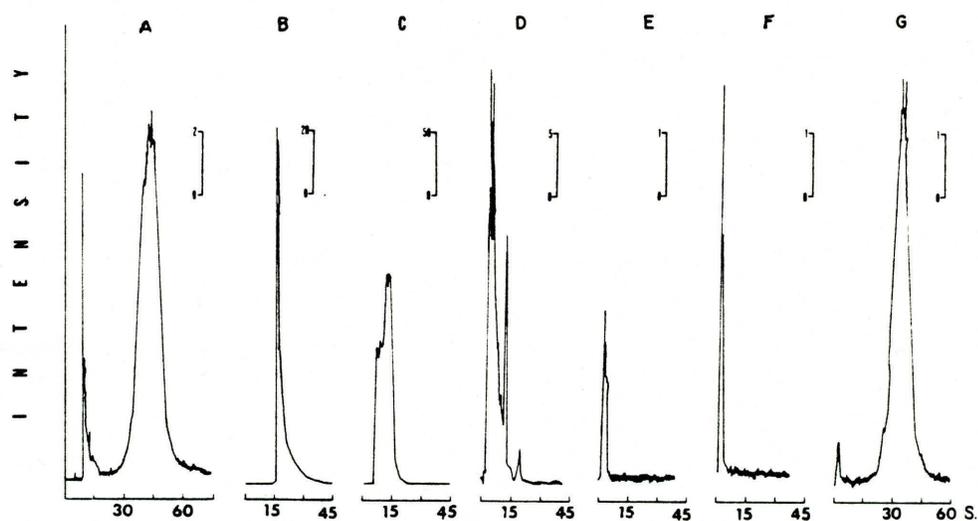


Figure 1.6. Emission spectra of sulfur-containing solids in the $H_2/Ar/air$ flame: A) 300 ppm of sulfur as PbS ; B) 600 ppm of sulfur as Na_2SO_4 ; C) 600 ppm of elemental sulfur; D) 40 ppm of sulfur as Na_2SO_3 ; E) 20 ppm of elemental sulfur; F) 40 ppm of sulfur as Na_2SO_3 ; G) 600 ppm of sulfur as CuS .

A, B, C, and D were obtained after the addition of 13 μL of the wetting solution containing H_3PO_4 . No wetting solution was added to solids in E, F, and G. All solid samples were prepared in SiO_2 .

TABLE 1.2. Comparison of MECA characteristics of solid sulfur containing compounds.

Compound	H ₂ /Ar/Air Flame		H ₂ /N ₂ Flame	
	No H ₃ PO ₄ added	H ₃ PO ₄ added	No H ₃ PO ₄ added	H ₃ PO ₄ added
	t _m (s)	t _m (s)	t _m (s)	t _m (s)
S ₈	2	12	4	20-22
PbS	2 35	12 45	5	27
CuS	2 40	15 60	7	20-22
Na ₂ SO ₃	2	4 12 17	5	1-5
Na ₂ SO ₄	--	17	--	>35

In the argon-cooled flame, the anion S^{2-} and SO_3^{2-} give a multi-peaked response. The first molecular emission from S^{2-} ($t_m \sim 12s$) arises from H_2S that is formed in the presence of an acid solution, and the second broad emission peak ($t_m > 40s$) probably arises from a polymeric sulfur species that is formed in the hydrogen flame. The three-peak sequence for SO_3^{2-} can be explained as follows: the first high intensity peak ($t_m = 4s$) arises from the SO_2 gas that is initially produced in the cavity. Subsequent reactions in the reducing flame can form species such as SH^- and H_2S which can give rise to the emission peak at $t_m = 12s$. The third peak at $t_m = 17s$, which is very weak, can be attributed to the small amount of SO_4^{2-} that is present in the solid Na_2SO_3 .

In the nitrogen-cooled flame, both S^{2-} and SO_3^{2-} show one peak. For SO_3^{2-} , the peak arises from SO_2 gas and the second peak found in the argon-cooled flame is not clearly defined. This observation can be rationalized if the concentration of SH^- or H_2S species in the nitrogen flame is lower than the concentration in the argon flame. The SO_4^{2-} concentrations in the SO_3^{2-} samples are small, and moreover, the sensitivity of the SO_4^{2-} determination is not as good as that in the argon-cooled flame, as shown later. It is not surprising therefore, that the SO_4^{2-} peak is not observed in the nitrogen-cooled flame. For S^{2-} , one peak is observed before the SO_4^{2-} peak appears in both the nitrogen-cooled and argon-cooled flames; however, the second peak is observed after the SO_4^{2-} peak, only in the argon-cooled flame. It was suspected that even after the sulfide sample had been converted into molecular sulfur in the

nitrogen-cooled flame, some sulfur-containing compounds remained in the sample compound. The samples that were converted into molecular sulfur in the nitrogen-cooled flame were subsequently heated in the argon-cooled flame; a second peak was observed at t_m values $>30s$.

Factors that Affect the Selectivity and Sensitivity of the Determination

Characteristics of Different Flames

The Emission Spectra of Different Flames. The emission spectrum of the H_2/N_2 /air at the optimized gas flow rate of 0.61, 2.4, 0.69 $L\ min^{-1}$ is shown in Figure 1.7. The emission spectrum of H_2/N_2 /entrained air at optimized gas rates of 0.61/2.4 $L\ min^{-1}$ and the emission spectrum of the H_2/Ar /entrained air and H_2/Ar /air at the optimized gas flow rate of 0.78/1.6/entrained air and 0.78/1.6/0.27 $L\ min^{-1}$ are also studied. The only significant difference is the OH emission band at about 306 nm. The other peaks are from the extraneous light in the laboratory. The OH band emissions at about 306 nm in these flames are shown in Figure 1.8. In the argon flame the OH peak is more intense than in the nitrogen flame.

The Maximum Temperature of the Sample Rod in Different Flames.

When the sample rod is placed in the flame, the temperature of the rod increases gradually and reaches maximum temperature. A type K thermocouple (Nickel-Chromium vs. Nickel-Aluminum) was attached to the sample cavity in the flame and the maximum temperatures attained in different flames were measured and summarized in Table 1.3.

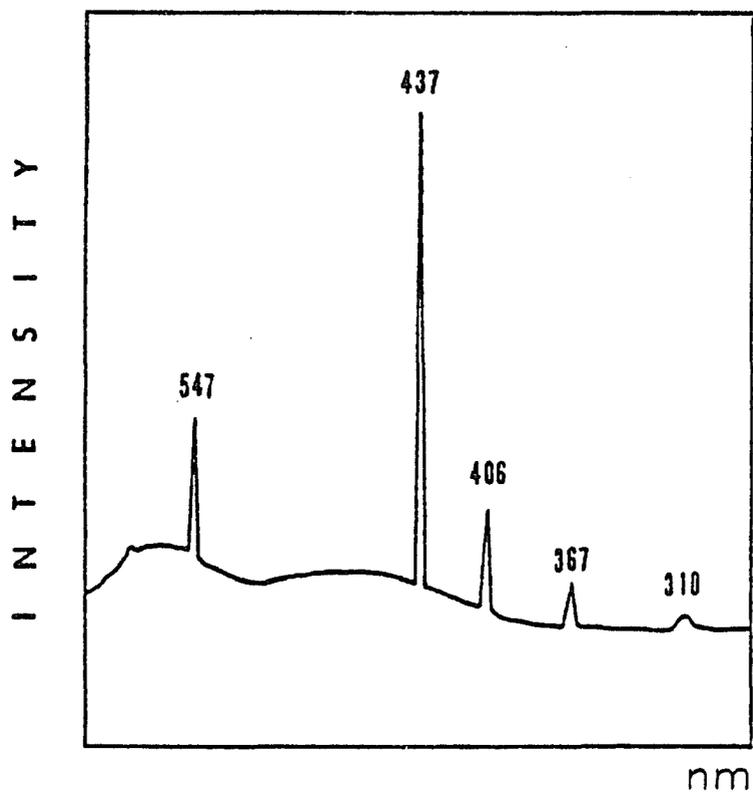


Figure 1.7. The emission spectrum of the H₂/N₂/air flame. All the peaks except the OH peak arises from the external illumination.

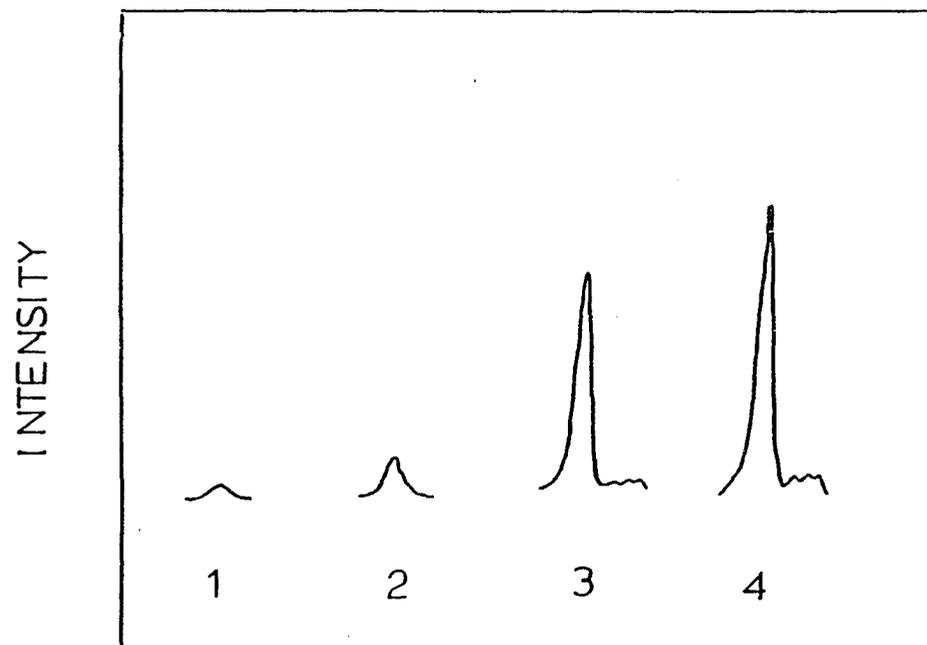


Figure 1.8. The OH band emissions of different flames (1) $\text{H}_2/\text{N}_2/\text{air}$; (2) $\text{H}_2/\text{N}_2/\text{entrained air}$; (3) $\text{H}_2/\text{Ar}/\text{air}$; (4) $\text{H}_2/\text{Ar}/\text{entrained air}$.

Table 1.3. Measured maximum temperatures for different flames.

<u>Flame (Flow Rate)</u>	<u>Maximum Temperature (°C) Measured</u>
N ₂ /H ₂ (2.4 L min ⁻¹ /0.61 L min ⁻¹)	390-400
N ₂ /H ₂ /air (2.4 L min ⁻¹ /0.61 L min ⁻¹ /0.69 L min ⁻¹)	465
Ar/H ₂ (1.6 L min ⁻¹ /0.78 L min ⁻¹)	450-460
Ar/H ₂ /air (1.6 L min ⁻¹ /0.78 L min ⁻¹ /0.27 L min ⁻¹)	470-490

The temperature measured in this manner is not corrected for radiation loss. The true temperature will be somewhat higher than the measured temperature. However, the aluminum cup in the cavity never melts (the melting point of aluminum is 660°C). This means that the temperature in the sample rod is less than 660°C . At the very least, it is known that the relative maximum temperature is obtained in the Ar/H₂/air flame is higher than in the N₂/H₂ flame. This agrees with the observation that shorter t_m values for the sulfur species are obtained in the argon-cooled flame than those obtained in the nitrogen-cooled flame.

Sample Cup Material

The results obtained from a series of simple experiments emphasized the importance of the sample cup material, especially in quantitative determinations of sulfur containing compounds by MECA. No sulfate emission band was observed in the H₂/Ar/air flame after the injection of 5 μL of a solution of 4×10^{-4} M H₂SO₄ and 5 μL of the wetting solution into a sample cup made of copper. If a platinum cup was used, the sulfate emission band was observed, but its intensity was enhanced by a factor of two when an aluminum cup was used. If the sample cup that was made from bright aluminum foil was first heated in the argon-cooled flame and then employed for the analysis, the intensity of the sulfate emission band was enhanced by an additional factor of about four. The surface of the aluminum cup, therefore, plays an important role in the promotion of the molecular sulfur emission.

Sample Rod Attachment

A 37 mm stainless steel extension tube was attached to the sample rod. When the edge of the tube was moved out gradually, the emission signal obtained with 4×10^{-4} M H_2SO_4 was decreased and the emission peak was broadened (Figure 1.9). No signal was observed when the edge of the tube was moved out to a distance of more than 5 mm. The sample rod attachment changes the flame environment near the sample cup. The temperature and the free radical concentrations are different. The t_m value shift is caused by the slower temperature increase of the sample rod. A better separation of different sulfur peaks may be obtained by using different sample rod materials which have slower heating rates.

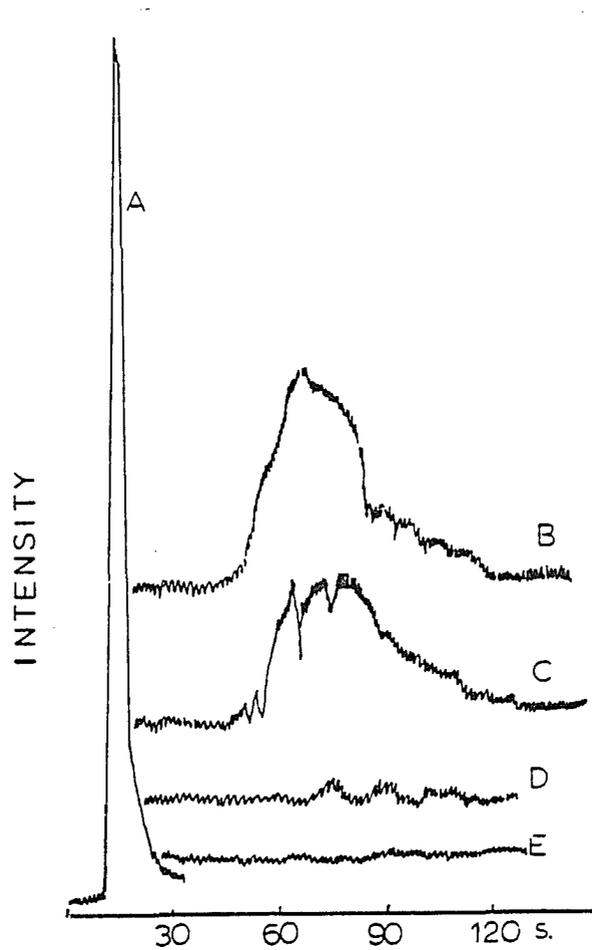


Figure 1.9. S₂ emission intensity under different conditions.
(A) No extension tube.
(B) to (E) extension tube was attached to the sample rod.
The edge of the tube was moved out (B) 2mm (C) 3mm (D) 5mm
(E) 7mm.

Determination of Mixtures of Sulfur Containing Species

Calibration Curves

The calibration curves for Na_2SO_4 , Na_2SO_3 , and PbS in an SiO_2 matrix are shown in Figure 1.10 to Figure 1.11. For Na_2SO_3 , the SO_4^{2-} peak is neglected and for S^{2-} the first peak is neglected. A calibration curve for elemental sulfur in nitrogen flame has not been obtained; however, the calibration curve for elemental sulfur in the $\text{Ar}/\text{H}_2/\text{air}$ flame is shown in Figure 1.12.

The following conclusions may be drawn by a comparison of these curves:

- a. The slopes are almost the same for the species in both argon and nitrogen flames. The slopes for Na_2SO_4 are 1.7 in the argon-cooled flame and 1.6 in the nitrogen-cooled flame. For Na_2SO_3 , the calibration lines show curvature. For PbS , the slopes are 1.0 in both flames for elemental sulfur, the slope in the argon flame is 1.5. The curvature of the sulfite calibration plot was caused by the increased loss of SO_2 , upon addition of the H_3PO_4 solution, with increasing amounts of Na_2SO_3 .
- b. The argon flame gave a higher sensitivity than the nitrogen flame. This can be deduced from the peak areas obtained for the same amount of sulfur in both the argon and nitrogen flame. In the argon flame, the detection limit (signal:noise ratio >2) for S_8 is 9 ng S/mg, for SO_3^{2-} it is 17 ng S/mg for SO_4^{2-} it is 5 ng S/mg, for S^{2-} is 16 ng S/mg. By using a nitrogen flame, it is difficult to determine 100 ng S/mg in a sulfate sample. The argon flame is far superior to the nitrogen flame in the determination of sulfate.

- c. The reproducibility of MECA is variable. If the calibration curve is obtained from the data collected on different days an average deviation of 25 percent is found for the determination of SO_4^{2-} in solid Na_2SO_4 and a 17 percent average deviation for the determination of SO_4^{2-} in aqueous H_2SO_4 . For some special cases, in which standards are diluted on the same day, the average deviation is reduced to 13 percent for solid sulfates and 8 percent for an aqueous sulfate solution.

The calibration curve for sulfuric acid has a smaller linear range than that for the solid sulfate as shown in Figure 1.13. The detection limit of sulfur in dilute sulfuric acid is less than 1.2 ppm in a 5 μL samples (or less than 6 ng S) in Ar/ H_2 /air flame if a used aluminum cup is employed. This is lower than the detection limit of 20 ng that has been reported by Belcher's group.

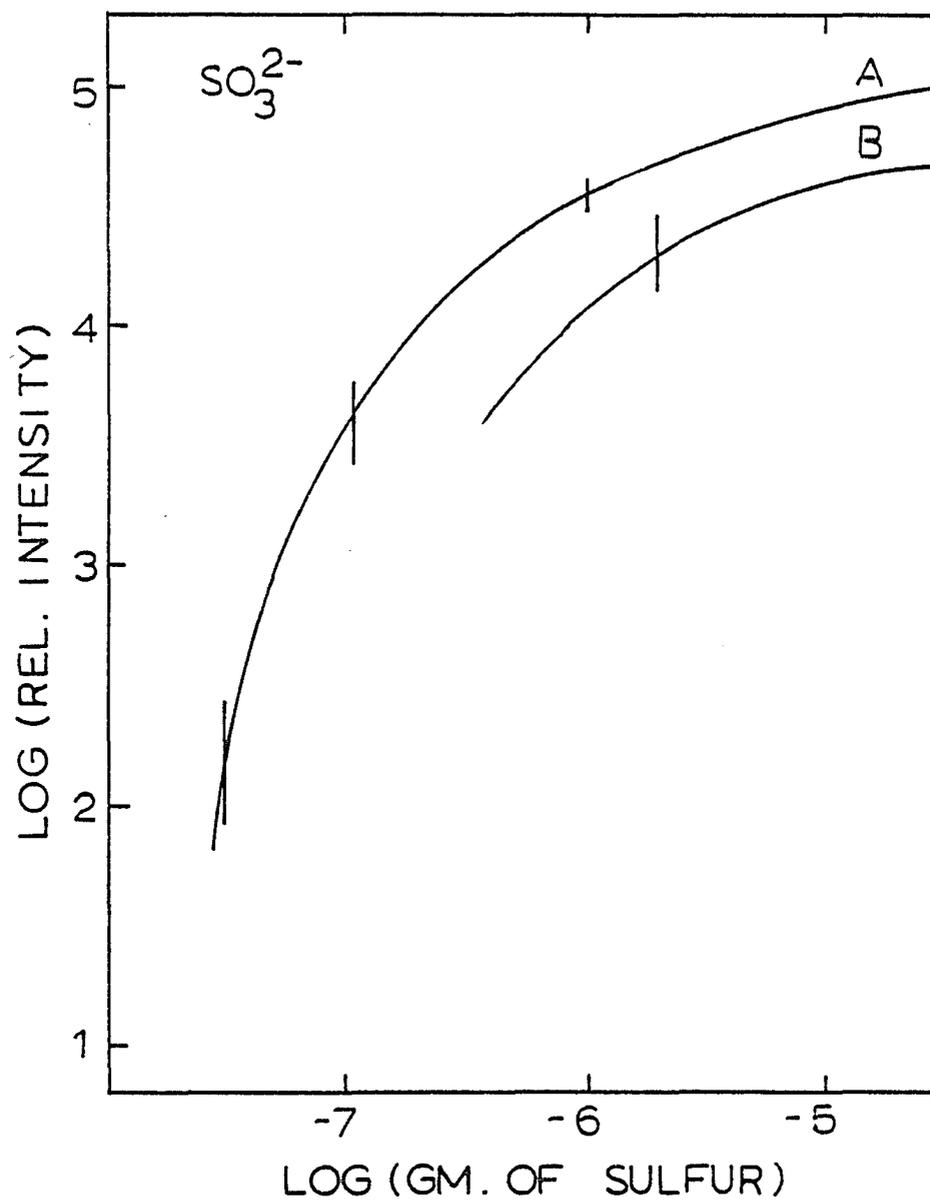


Figure 1.10. Calibration curves of SO_3^{2-} (A) in $\text{Ar}/\text{H}_2/\text{air}$ flame. (B) in N_2/H_2 flame.

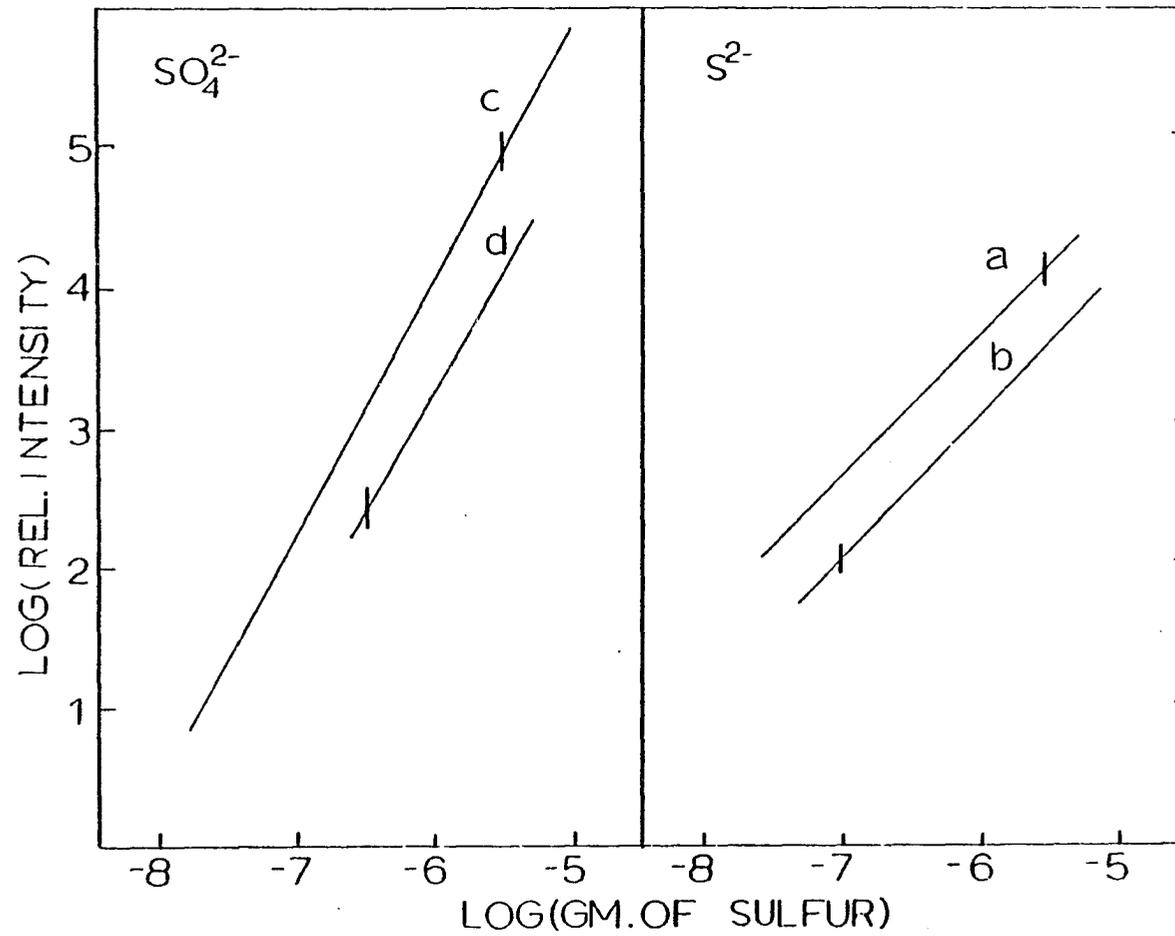


Figure 1.11. Calibration curves of S^{2-} and SO_4^{2-} . S^{2-} in (a) Ar/H₂/air flame and (b) N₂/H₂ flame, SO_4^{2-} in (c) Ar/H₂/air flame, and (d) N₂/H₂ flame.

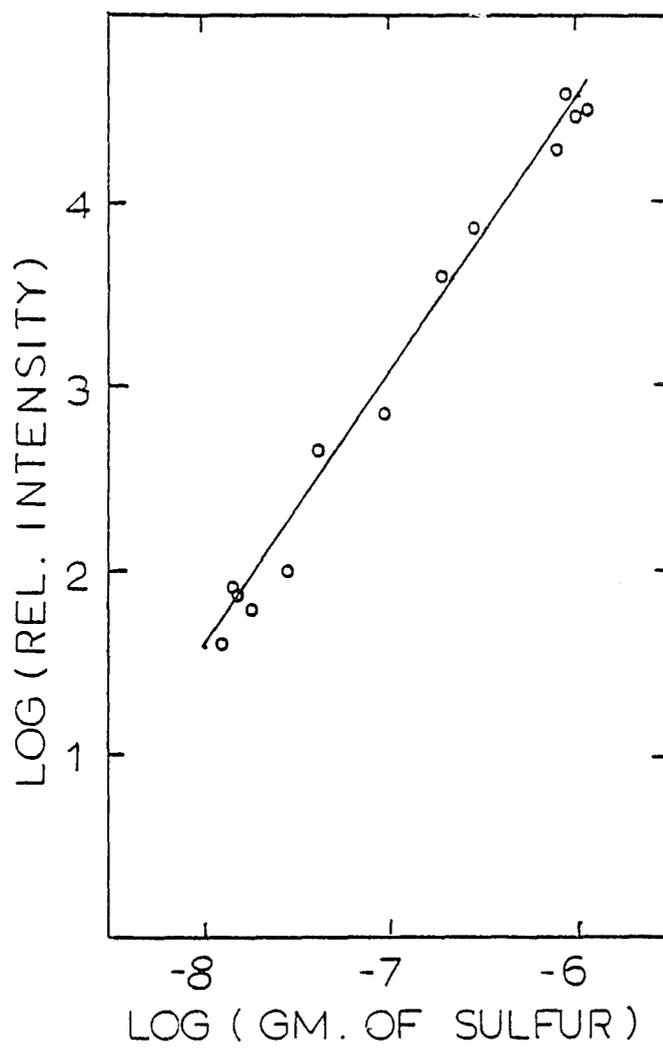


Figure 1.12. Calibration curve of S_8 in Ar/H₂/air flame.

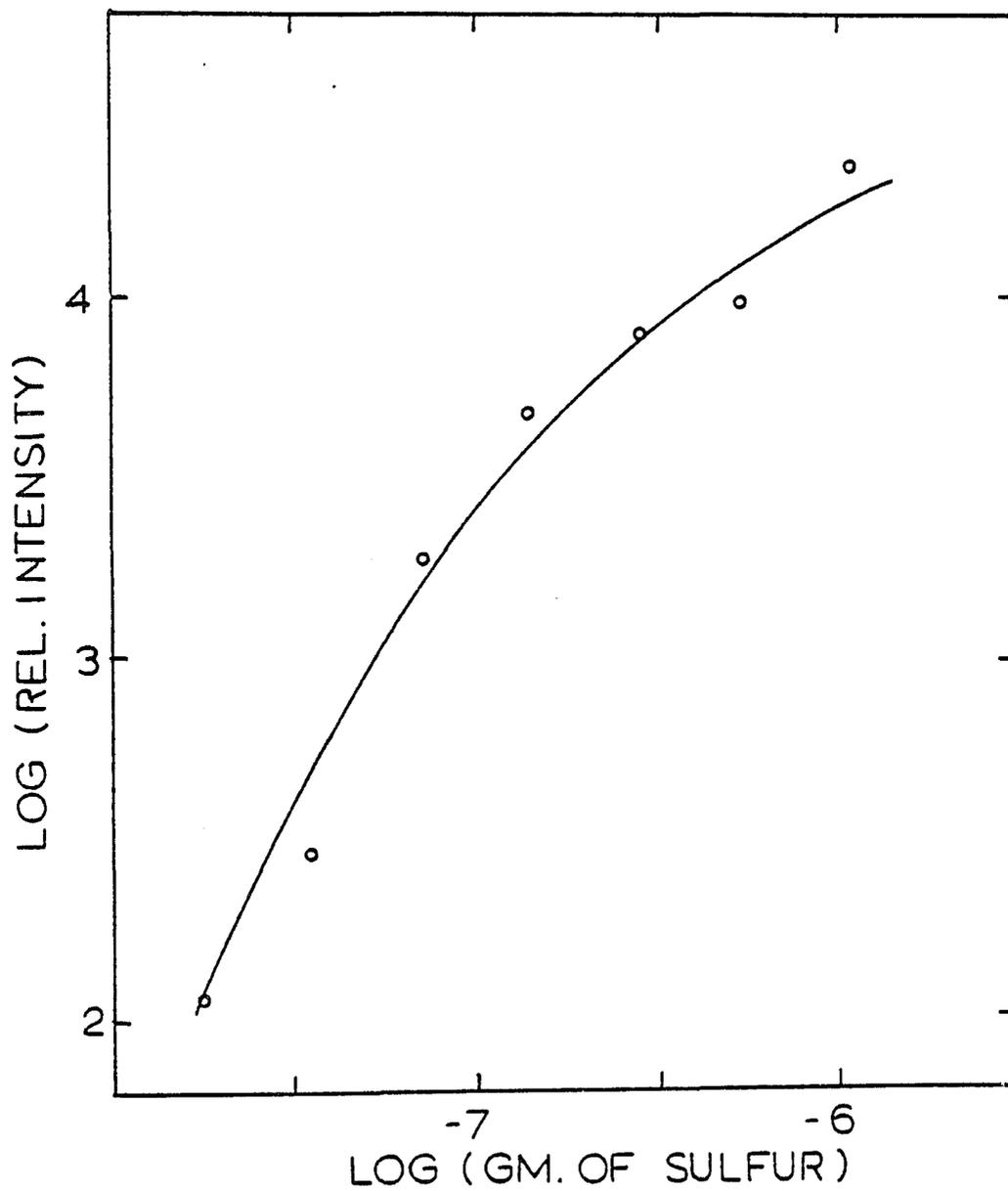


Figure 1.13. Calibration curve of H_2SO_4 in aluminum cup in which H_3PO_4 was heated previously in an Ar/ H_2 /air flame.

Determination of S^{2-} , SO_3^{2-} , and SO_4^{2-} in a Mixture

It is possible to determine S^{2-} , SO_3^{2-} , and SO_4^{2-} simultaneously with the aid of the Ar/H₂/air flame. The results are summarized in Table 1.4. The average deviation is almost the same as that obtained with the N₂/H₂/extrained air flame which was used by Schubert to analyze various mixtures of sulfur containing species (Table 1.5) (12).

Calibration curves from the cumulative data were used in this determination. It is possible to obtain better precision by running the standard and the unknown on the same day.

The determination of S^{2-} , SO_3^{2-} , S_8 , and SO_4^{2-} in a mixture with a single sample determination has been reported by Schubert, and will not be repeated here.

The relative average deviation for six samples is only three percent, and the high values for S^{2-} in a mixture containing S^{2-} , SO_3^{2-} , and SO_4^{2-} are probably due to the difficulty in obtaining a representative sample.

Table 1.4. Determination of S^{2-} , SO_3^{2-} , and SO_4^{2-} in mixtures in argon-cooled flame.

Mix.	Species	True (ppm)	Measured (ppm)	Mean (ppm)	Relative Average Deviation (Percent)	Average Deviation From True (Percent)
1	SO_4^{2-}	269	236,264,274,268	261	4	3
	SO_3^{2-}	333	387	387		16
2	SO_3^{2-}	332	197,210	204	3	39
	S^{2-}	275	362,209	286	27	4
3	SO_4^{2-}	284	181,158,282,103	181	28	64
	S^{2-}	316	329,549,538,356	443	22	40
4	SO_4^{2-}	307	210,402,289,396, 301,299	300	22	2
	SO_3^{2-}	345	221,734	478	54	38
	S^{2-}	328	873,840,915 826,354,583	876	3	167

Table 1.5. Sulfur content of particulate samples collected at three stages of a copper smelting facility.

Sample	Wt% S^{2-} ^a	Wt% SO_3^{2-} ^a	Wt% SO_4^{2-} ^a	Total Wt% S
Ore Dust	0.69 ± 0.23	n.d. ^b	10.2 ± 1.6	4.1 ± 0.6
Roaster Dust	0.32 ± 0.10	0.024 ± 0.008	3.2 ± 0.9	1.40 ± 0.31
Converter Dust	0.086 ± 0.010	0.006 ± 0.004	2.4 ± 0.4	0.89 ± 0.15

^a Uncertainties represent standard deviations for five determinations.

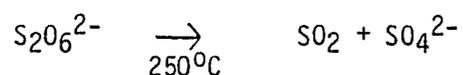
^b n.d. = not detected.

Determination of Sulfate in Samples of Ferromanganese Nodules Treated with SO_2 (15)

The sulfate content of samples of ferromanganese nodules treated with SO_2 was determined by the MECA technique. The emission peak obtained with the solid samples are shown in Figure 1.4. When the finely ground solid samples were diluted by a factor of 100 to 1,000 by the addition of solid SiO_2 , as described previously, a sharp peak with a t_m value identical to that given by the SO_4^{2-} species was obtained (Figure 1.18).

The following experiment was carried out to prove that the sulfur species in SO_4^{2-} and not $\text{S}_2\text{O}_6^{2-}$: Two samples were selected and heated to 250°C overnight in an oven. No significant differences were found in the MECA peaks obtained with the heated samples and the samples that were not heated.

If the sample contained $\text{S}_2\text{O}_6^{2-}$, the emission signal should decrease in intensity as a result of the following reaction:



The results of the determinations are shown in Tables 1.6 and 1.7. Again, the calibration curve from the cumulative data sets was used, and gave an average deviation of 20–30 percent.

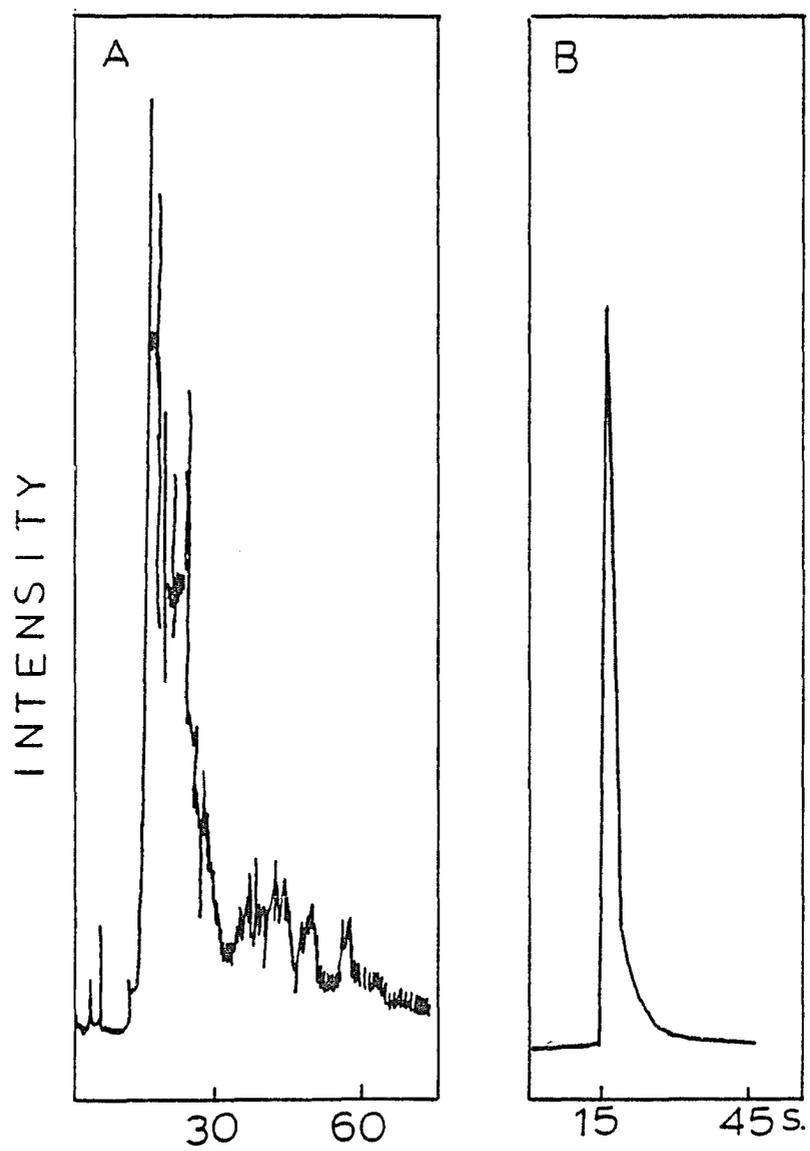


Figure 1.14. Signals of undiluted (A) and diluted (B) nodule samples.

Table 1.6. Determination of sulfate for SO₂ treated nodules.

Sample	Number of Determination	Average Percent of Sulfur Found	Average Deviation (Percent)
II-1-K	3	16.13 \pm 4.03	25
II-1-V(e)	3	12.56 \pm 4.40	35
II-2-K(e)	3	7.03 \pm 1.55	22
RC9-T1 (Sulfated)	3	8.46 \pm 2.28	27
KK-77 (Sulfated)	2	10.50 \pm 2.00	19
SEDCO 445 (Sulfated)	3	18.52 \pm 4.63	25

Table 1.7. Comparison of heated and unheated samples.

Sample	Number of Determinations	Average ppm	Average Relative Deviation (%)
dil. RC9-T1 (heated 250°)	3	286 \pm 17	6
dil. RC9-T1	3	235 \pm 6	3
SEDCO dil. (heated 250°)	3	234 \pm 83	35
SEDCO dil.	3	296 \pm 45	15

Sulfur Species in Coal Samples

The determination of total sulfur and the various sulfur forms that are found in coal is an important but formidable analytical problem. The recommended method that has gained wide acceptance for routine laboratory use is Walker and Hartner's method (16). In this method the SO_4^{2-} , which is usually less than 0.05 percent, is determined as BaSO_4 after the coal is extracted with dilute HCl . The pyritic sulfur, mainly found as FeS_2 , in the residue from the HCl extraction is dissolved in dilute HNO_3 and the iron in solution is determined by permanganate titration. The pyritic sulfur is calculated from this iron determination and the organic sulfur is calculated as the difference between the total sulfur, determined by the ASTM method (17), and the sum of the sulfate sulfur and the pyritic sulfur.

A sample of coal (K-95007) was obtained from the Department of Energy and the following analytical data were provided for this sample: total sulfur 3.28 percent; organic sulfur 0.86 percent; pyritic sulfur 2.40 percent; and sulfate sulfur 0.02 percent. The MECA emission spectra in the argon-cooled and in nitrogen-cooled hydrogen flame are shown in Figure 1.15. The emission bands occur in three regions in the argon-cooled flame: a) $t_m < 10$ s; (b) $10 \text{ s} < t_m < 15$ s; and (c) $15 \text{ s} < t_m < 25$ s. The molecular sulfur emission bands, in the region, $t_m < 10$ s, arise from organic sulfur species that are present in coal. If the coal is exhaustively extracted with CHCl_3 , and the MECA spectrum of the residue is obtained, the peaks in region (a) are eliminated and the peak intensities in region (b) are diminished considerably. This indicates that some of the organic

sulfur species contribute to the emission bands in the region $10 \text{ s} < t_m < 15 \text{ s}$. The main contribution to the emission spectrum in this region is from the pyritic sulfur. The Walker and Hartner method for the determination of sulfate sulfur in coal is based on its extraction with dilute HCl. This dissolves the sulfate sulfur and leaves the pyritic and organic sulfur in the insoluble residue. Analysis of this residue by MECA indicated that some organic sulfur was also dissolved in the extraction step with dilute HCl because the emission band intensities in region (a) were considerably reduced. Whether some of these solubilized organic sulfur containing species are eventually converted into SO_4^{2-} is not known. It is important to identify all the soluble sulfur containing species in the dilute HCl extract before any valid claims are made about the Walker and Hartner method for the determination of sulfate sulfur in coal.

It was observed that the intensity of emission band from sulfate sulfur in region (c) ($15 \text{ s} < t_m < 25 \text{ s}$) was considerably lower in the argon-cooled flame than in the nitrogen-cooled flame (Figure 1.15). This is a direct contradiction of the previous experimental results which showed that the argon-cooled flame is much more sensitive than the nitrogen-cooled flame for the determination of SO_4^{2-} in solids. A plausible reason for the reduced sensitivity in the argon-cooled flame is that in solid matrices, such as coal, which contain a large amount of carbon, reductive processes occur in the high temperature region of the MECA cavity with the formation of species containing sulfur in lower oxidation states.

The results of our preliminary experiments with coal have shown that it is not possible to determine the various forms of sulfur in this complex matrix by employing the usual MECA procedures. Successive extraction steps must be carried out with organic solvents, dilute acids, and mixtures of acids. All sulfur species that are in the residue and that are in solution must be identified after each extraction step. In addition to the many variables in the MECA technique, the flame temperature will have to be controlled to minimize reductive processes that can occur in the presence of carbon.

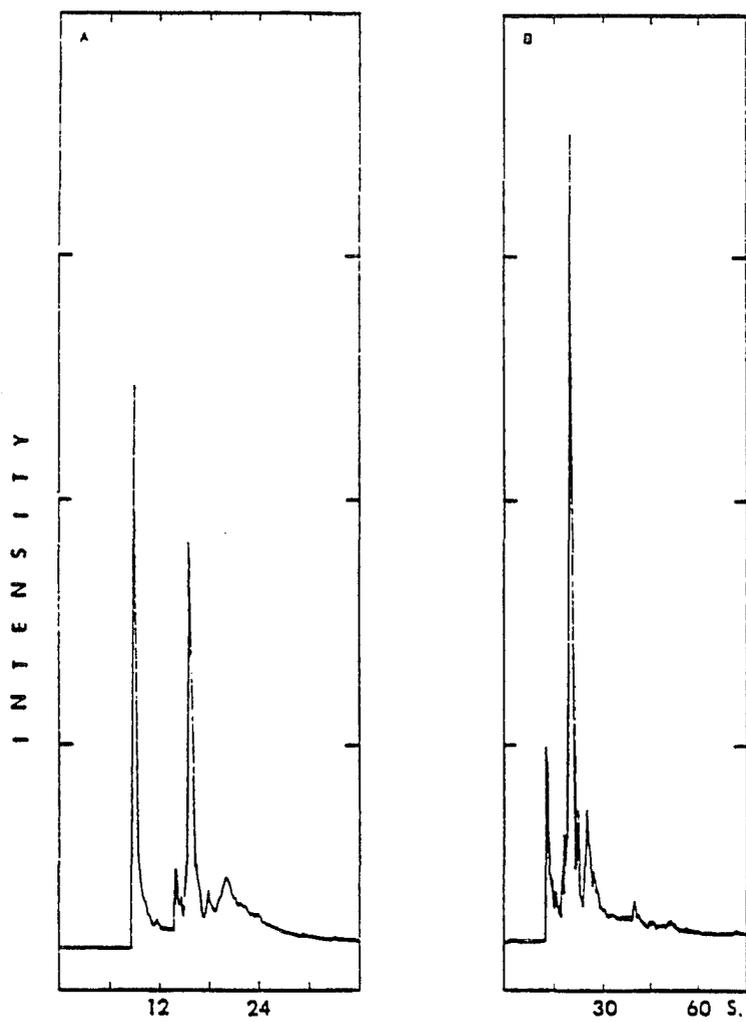


Figure 1.15. MECA emission bands of coal in the argon-cooled flame (A) and nitrogen-cooled flame (B).

Discussion

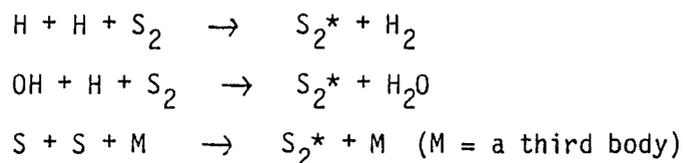
By using the Ar/H₂/air and the N₂/H₂/entrained air flame, with the MECA technique we can determine elemental sulfur and sulfide, sulfite and sulfate anions in a solid mixture. The argon-cooled flame is much more sensitive than the nitrogen-cooled flame, and is especially useful for the determination of sulfate in a variety of solids which do not have to be dissolved. The emission bands that arise from elemental sulfur and sulfide overlap to a great extent in the nitrogen-cooled flame, but are well separated in the argon-cooled flame. An advantage of the nitrogen-cooled flame, however, is that the emission bands from sulfite and elemental sulfur are well resolved.

The reproducibility of the measurements varied from 10 to 30 percent. The main reason for this poor reproducibility is the non-homogeneity of the samples (1-2 mg) of the solid standards that were prepared by serial dilution with solid SiO₂ and analyzed in the MECA sample cup. Additional reasons for the poor reproducibility are the variable surface composition and the geometric differences in the aluminum sample cup, cooling water flow rate which has never been controlled precisely, and possible loss of sample when rotating the sample rod into the flame, and the difficulty in positioning the sample rod in a reproducible manner in the flame. Since about 10 percent average deviation was found for aqueous dilute sulfuric samples, the non-homogeneity of the solid sample is not the only reason for the poor reproducibility. In order to obtain a better reproducibility, standards and samples should be alternated during the course of series

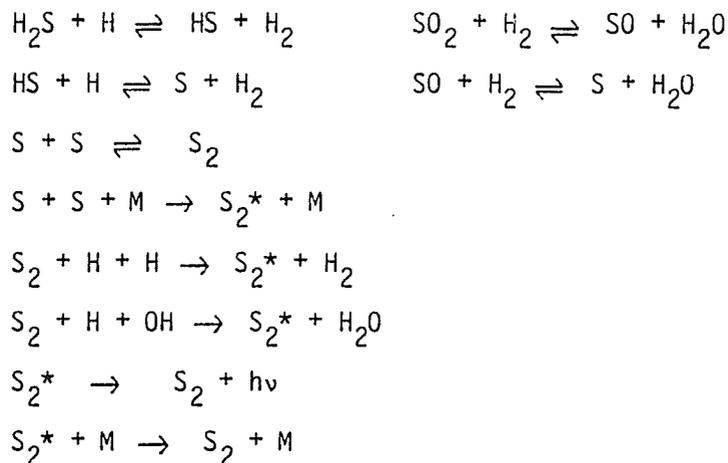
of experiments. The use of a larger burner may reduce the problems associated with sample non-homogeneity.

Differences in the t_m values depend on the differences in the physical properties of the compounds, e.g., boiling point, sublimation temperature, and the manner in which the compound thermally decomposes. Sulfites decompose at red heat and, therefore, the molecular emission from sulfites is observed at low t_m values. Elemental sulfur melts readily ($\sim 113^\circ\text{C}$) and may decompose to form H_xS_y species in the hydrogen flame and the molecular emission from elemental sulfur is observed after the formation of these species. After the addition of H_3PO_4 , H_2SO_4 is released from Na_2SO_4 . Since the boiling point of H_2SO_4 is at 330°C , the molecular emission from sulfates is observed at t_m values greater than those for elemental sulfur. Sulfides may form polysulfides and consequently the emission bands are broadened. All these compounds are converted into SO_2 , H_2S , S_8 , etc. in the flame. Muller et al. (18) have described a series of 36 reactions that can occur in the flame.

The proposed excitation mechanisms are (19,20):



A simplified mechanism for the molecular emission that is obtained from sulfur containing species is as follows:



Where M is a third body, such as the surface of the aluminum sample cup.

The preceding results indicate that the temperature of the argon-cooled flame is higher than that of the nitrogen-cooled flame. The additional observation, that the intensity of the S_2 emission is greater in the argon-cooled flame may be the result of a decrease in the quenching or an increase in the concentration of OH radicals in the flame that increase the concentration of excited state S_2 species by collisional processes. From the S_2 spectrum we have obtained all the peaks that arise from $v = 0$ in the excited state to $v = 7, 8, 9, 10$ in the ground state. This means that probably, all states in which $v > 0$ are converted to $v = 0$ in the excited state by collisional processes; emission occurs when this excited state ($v = 0$) goes to the ground state.

Future Research

It would be of interest to determine the concentrations of the species in the MECA cavity by molecular beam mass spectrometry (21,22). The stable species in the flame can be sampled by means of a fine quartz

probe, the tip of which is located at an appropriate position in the flame. The species pass through the specially shaped orifice of the probe and into the mass spectrometer, the pressure in the sampling orifice being reduced from that of the flame to the operating pressure of the spectrometer (about 10^{-5} - 10^{-6} mm Hg). An intermediate (or differential) pumping stage may be employed between the orifice and ionization chamber to give greater control over this pressure decrease. In some of the sampling techniques species were passed from the probe into a previously evacuated flask, from which a small sample was admitted into the spectrometer.

Introduction of the probe may cause a change in the normal behavior of the flame, since the probe may disturb the natural flow of the flame gases and hence give a false picture of the species present at the point of sampling; or the probe surface may act catalytically on the species present. Distortion of the flame can be minimized by using a probe of small diameter which is aligned along the streamlines of the flame and has a small orifice (theoretically, the distance over which the flame is disturbed during sampling is 20-30 times the diameter of the orifice, which is generally 20-50 microns). Catalytic effects on probe surfaces are generally considered to be small provided the probes are constructed of an inert material such as quartz, and are properly cleaned. However, it depends on the composition of the species—elements such as sodium will readily react with a quartz probe at flame temperatures. Generally, mass-spectrometric analyses of stable species have given reasonable self-consistent, and reproducible results.

Destruction of radicals before analysis could take place, either by recombination or by reactions at the walls of the apparatus between the entrance orifice and the ionization chamber. This problem has not yet been overcome satisfactorily. In order to minimize it, the path of the radicals between production and introduction into the ion source is kept as short as possible. However, this is very difficult for flames burning at atmospheric pressure because of the increased path length from the flame to the mass spectrometer while the pressure is being reduced sufficiently for entry into the ionization chamber.

Recently, laser methods have been used to measure species concentrations and temperatures for a wide variety of molecules over a range of conditions, and has been successfully accomplished with high spatial resolution. In general, the lasers form a nonintrusive probe which do not perturb the gas flow or chemical reactions, although the use of a high intensity laser can create a significant excited state population in the species it is pumping, it causes complications due to differences in reactivity between excited and ground states.

Laser-induced fluorescence (LIF) depends on the absorption of photons by molecules and detection limits of sub-ppb can be achieved. This method is suitable for measurement of those minor species which are the transient intermediates in a reaction network. Muller et al. (23) have used LIF to study the concentrations of S_2 , SH, SO_2 , OH in the one percent H_2S that is present in a $H_2/O_2/N_2$ flame. It is possible to use this technique to measure species of interest in the MECA flame near the sample rod tip and to determine the relationships

between the concentration of these species and the S_2 emission intensity. From these relationships, a clearer picture of the flame chemistry may be obtained.

Future work should also be directed at identifying species that interfere with the molecular emission of sulfur. Separation techniques for the removal of interferences and the use of masking and complexing agents is a fruitful field for future investigation.

Non-flame techniques constitute another approach that may yield useful results. Excited He (24), or active nitrogen (25) or hydrogen (26) atoms generated by electrodeless radio-frequency discharges may be employed to study the emission of S_2 species in the gas phase.

The identification of various organic sulfur species and all the sulfur species in coal are challenging problems that should be investigated with the MECA technique.

Summary

In summary, the only method that is available for the quantitative determination of S_8 , S^{2-} , SO_3^{2-} , and SO_4^{2-} at ppm levels in milligram quantities of solid samples, is MECA. The method is simple and rapid and, despite its shortcomings, it can be employed to determine each or all of these sulfur containing species in solid samples by the judicious use of the nitrogen-cooled flame and the argon-cooled flame. For example, SO_3^{2-} in a solid sample is best determined by measurement of the peak area of $t_m \leq 5$ s in a nitrogen-cooled flame and trace levels of SO_4^{2-} in solids are readily

determined by measurement of the peak area at $t_m = 17s$ in an argon-cooled flame. The overlap of S^{2-} and S_8 in the nitrogen-cooled flame can be well separated by the use of the argon-cooled flame.

CHAPTER 2

SYNTHESIS AND IDENTIFICATION OF COPPER(I) COMPOUNDS FORMED BY THE REACTION OF SULFUR DIOXIDE WITH AMMONIACAL SOLUTIONS CONTAINING COPPER(II)

Introduction

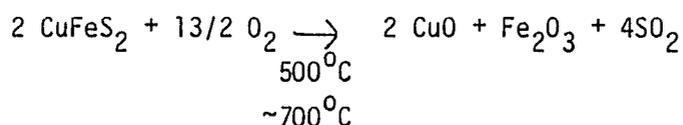
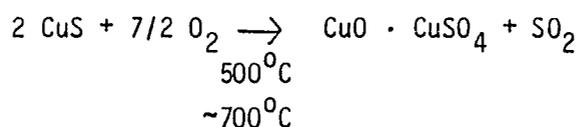
Copper is present in the earth's crust mainly in the form of sulfide minerals such as chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), and chalcocite (Cu_2S). The concentration of these minerals in an ore body is low: typical copper ores contain 0.5 percent to 2 percent copper. The sulfide ores are concentrated by flotation, roasted and smelted to give blister copper which is finally electro-refined to give copper metal (27).

Copper also occurs in the form of oxidized minerals (carbonates, oxides, silicates, sulfates), but to a much lesser extent. Ores containing these minerals are almost always treated by hydrometallurgical methods since the oxide ores presently being mined are too lean in copper for direct pyrometallurgical reduction. In addition, most oxide minerals cannot be efficiently concentrated by froth flotation and they are, therefore, more effectively treated by hydrometallurgical techniques, i.e., by leaching with sulfuric acid followed by precipitation or electrowinning of the copper from solution.

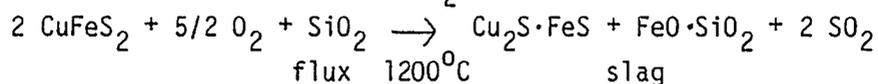
The copper obtained by cementation (precipitation with scrap iron) is contaminated with iron and it is usually retreated by pyrometallurgical methods.

There is an alternative way to obtain copper after the ore has been leached with sulfuric acid, i.e., reduction of copper(II) in an ammoniacal solution by the use of gaseous sulfur dioxide to form crystalline solids which can be converted to elemental copper and copper(II) by the addition of sulfuric acid at room temperature or to elemental copper at higher temperatures (140°C to 170°C) and pressures from 150 to 220 psi. The elemental copper obtained by this route has a purity better than 99 percent. This method of copper production has several advantages: power requirements are minimal if further purification by electrowinning is not necessary, and the required sulfur dioxide can be obtained from the roasting and smelting of sulfide ores, as shown below.

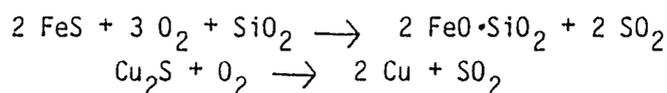
Roasting to eliminate sulfur:



Smelting to form copper matte ($\text{Cu}_2\text{S} \cdot \text{FeS}$):



In the converting process in which the liquid matte is oxidized:



blister copper (98.5 percent Cu)

The only reactant that is required, besides sulfur dioxide, in the aqueous reduction process is ammonia. Its expense can be offset by the production of ammonium sulfate which can be used as a fertilizer. In addition to the economics of the production of copper, there is the environmental benefit of using the unwanted sulfur dioxide. Although the above mentioned method has been known, and even used on a pilot scale for many years, little fundamental information is available on the chemical reactions and the intermediates that are formed. For example, the crystalline solids formed by adding SO_2 to Cu(II) ammoniacal solutions have not been studied in any detail. Porth et al. (28) have considered that these solids may contain the compounds CuNH_4SO_3 and $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$. In this study, Porth's synthetic methods has been adopted and the crystalline solids that are formed have been identified. It is expected that the identification of these compounds will help to devise a more efficient route for the production of high purity copper.

Synthetic Methods

Sulfur dioxide from a tank is passed through a wash bottle which contains an ammoniacal copper(II) solution. The excess sulfur dioxide gas that is unreacted is trapped in an aqueous sodium hydroxide solution.

Copper(II) sulfate pentahydrate was dried for two hours at 110°C in an oven and cooled in desiccator before use. A certain amount of the cupric sulfate was weighed and dissolved in distilled deionized water. Concentrated aqueous ammonia was added to the

copper(II) solution while the solution was stirred continuously and its pH was monitored. The precipitate that was formed initially redissolved in a slight excess of ammonia. The pH of the purple-blue solution was controlled between 9.5 and 10.5. Sulfur dioxide was passed through this solution until a precipitate was formed. The color of the precipitate changed from yellow to green, to brown, and finally to a shiny pink. The solution changed from purple to blue to green and finally to a pale green color. The pH of the solution was measured again and the solution and precipitate were allowed to stand for several days. The solution was decanted and the precipitate was separated by filtration. The precipitate was washed with water and dried in vacuo at room temperature for several hours and stored in a desiccator.

All the experimental data are summarized in Table 2.1. The abbreviations used are: G = green, R = red; Y = yellow; CL = colorless; L = light; D = dark; X = crystals washed with water; Crystal I = dark red brown crystal with dimensions 500 X 300 X 300 μm ; Crystal II = colorless, square plates with dimensions about 10 X 10 μm ; Crystal III = colorless, hexagonal plates with dimensions about 10 X 10 μm ; Crystal IV = colorless, three dimensional crystal about 100 X 100 X 10 μm ; Crystal V = brown, rhombohedral crystal with dimensions about 15 X 15 X 10 μm . All colors described are the colors seen under a low-power microscope.

Chemical Analysis

Methods

The sulfur-species present in the crystals were determined by the MECA. Samples were diluted with silicon dioxide before they were introduced into the flame.

About 0.5 gram of each sample was used for determination of the percent of nitrogen in the compounds by Kjeldahl's method. BO_2^- , formed from the reaction of NH_3 and HBO_2 , was titrated with standard HCl.

Oxidation of the Samples

About 0.7 gram of each sample was treated with bromine water until any precipitate that formed was dissolved. The solution was heated on a hot plate to remove the excess bromine in the solution. This oxidation converted all the sulfur species into sulfate which was determined by precipitation as BaSO_4 . The copper(II) in solution was determined by atomic absorption spectrophotometry. The percentage of water of hydration in the samples was obtained by difference.

Results

Sample numbers 2, 3, 8, and 10 formed only one type of crystal and were selected for chemical analysis. The results are summarized in Table 2.2. The calculated values for compounds of known stoichiometry are also included for comparison.

Discussion

Five types of crystals were obtained in the course of the synthesis. These crystals were left in the mother liquor for several days until they had grown to a sufficient extent. It was found that crystal type 2 had a tendency to change to crystal type 1. An unstable compound which has greyish color was formed as an intermediate compound when crystal type 2 changed to crystal type 1. This intermediate compound is unstable and could not be separated for identification.

Crystals of type 4 appear to be green by reflected light, although they are colorless when viewed under the microscope by transmitted light. These crystals were formed with several other types of crystals and a sufficient number of type 4 crystals could not be obtained for elemental analysis. However, a single crystal of type 4 was separated and x-ray diffraction data were collected. The cell constants were the same as those reported for the compound: $(\text{NH}_4)_2[\text{Cu}(\text{H}_2\text{O})_6][\text{CuSO}_3]_4$, i.e., $a = b = 14.876$; $c = 17.218$, $\alpha = \beta = \gamma = 90^\circ$ (29). The description of this compound as well as its density, (2.72 g cm^{-3}) are identical with those of the type 4 crystal.

Crystals of type 3 and 5 had the same composition, although their physical appearance was different.

Okabe et al. (30) reacted different amounts of $(\text{NH}_4)_2\text{SO}_3$ with CuSO_4 and obtained several kinds of crystals. They were reported as follows: $7 \text{ Cu}_2\text{SO}_3 \cdot 2 \text{ CuSO}_3 \cdot 3 (\text{NH}_4)_2\text{SO}_3 \cdot 24 \text{ H}_2\text{O}$ —colorless, transparent, square, thin plates, or an aggregate of

spherical microcrystals observed as a yellow-green powder by the naked eye. It is slowly converted to Chevreul's salt, $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$, in the presence of a low concentration of copper(II). $\text{Cu}_2\text{SO}_3 \cdot 7(\text{NH}_4)_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$ —transparent, colorless needles, very soluble in water. $\text{Cu}_2\text{SO}_3 \cdot 7(\text{NH}_4)_2\text{SO}_3 \cdot 9\text{H}_2\text{O}$ —tetragonal, soluble in water, it is formed from a pale wine-red solution. $\text{CuSO}_3 \cdot (\text{NH}_4)_2\text{SO}_3$ —rhombohedral, insoluble in water and stable in air. Bipyramidal crystals are formed in the presence of zinc ions, and hexagonal plates in the absence of zinc ions. $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ —pseudo orthorhombic, insoluble in water, but slightly soluble in sulfurous acid. This compound is always formed readily in the presence of a low concentration of ammonium sulfite, or in a relatively high concentration of ammonium sulfite, via the intermediate compound, $7\text{Cu}_2\text{SO}_3 \cdot 2\text{CuSO}_3 \cdot 3(\text{NH}_4)_2\text{SO}_3 \cdot 24\text{H}_2\text{O}$.

From the above information and the analytical results, the five crystals are assigned the following stoichiometry:

Crystal I: Chevreul's salt, $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$

Crystal II and IV: $(\text{NH}_4)_2[\text{Cu}(\text{H}_2\text{O})_6] [\text{CuSO}_3]_4$

Crystal III and V: $\text{Cu}_2\text{SO}_3 \cdot (\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$

The experimental data that were collected indicated that the formation of Chevreul's salt was favored in the presence of low ammonia concentrations. The presence of high ammonia concentrations favors the formation of other compounds, such as II and III. On the basis of x-ray crystallographic results, crystals of type 2 and type 4 were assigned the stoichiometry $(\text{NH}_4)_2[\text{Cu}(\text{H}_2\text{O})_6] [\text{CuSO}_3]_4$ instead

of $7 \text{Cu}_2\text{SO}_3 \cdot 2\text{CuSO}_3 \cdot 3(\text{NH}_4)_2\text{SO}_3 \cdot 24 \text{H}_2\text{O}$ which was reported previously by Okabe et al. Recently the magnetic moment values (μ) of crystals I and II have been determined (31). The value of μ for crystal I was 1.80 B.M. for the chemical formula $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2 \text{H}_2\text{O}$ and μ of crystal II was 1.90 B.M. for the chemical formula $(\text{NH}_4)_2[\text{Cu}(\text{H}_2\text{O})_6][\text{CuSO}_3]_4$. These values showed there was one unpaired electron, i.e., one Cu(II) in each molecule, in both types of crystals. This is in agreement with our conclusions.

Future work will be directed towards the following:

1. A wider range of SO_2 and NH_3 concentrations will be used with the expectation that other Cu(I) intermediates may be isolated.
2. The mechanisms involving the reduction of each of the Cu(I) compounds that have been identified should be investigated.
3. The optimum solution conditions under which this reduction can be most efficiently carried out should be determined.

Table 2.1. Synthesis results.

Sample Number	CuSO ₄ (g)	H ₂ O (ml)	pH		Color ^c		d	Color ^e		Wash	Crystal
			NH ₃ ^a	SO ₂ ^b	Soln	ppt		Soln	ppt		
1	1.235	100	9.77	3.44	G	GBW	7	G	DRB	X	I
2	1.220	100	9.93	3.10	LG	GBW	15	G	DRB	X	I
3	1.306	100	10.02	3.52	LG	GBW	7	CL	G	X	II
4	1.136	100	10.10	4.50	CL	GBW	15	CL	WG	X	II
5	1.077	100	10.20	3.23	CL	PB	15	CL	WG, LB	X	II, III, IV, V
6	3.109	100	10.32	3.40	LG	GBW, B	15	LG	G, LB	X	IV, V
7	3.349	100	10.11	2.30	LG	GBW, B	15	LG	WG, DBP	X	II, III, IV
8	3.445	100	10.14	5.35	CL	B	7	CL	YB	X	V
9	4.464	100	9.74	3.03	CL	R, B	15	CL	LB, B	X	V
10	3.266	400	9.99	4.01	CL	PB	5	CL	PB	X	III
11	4.010	800	9.99	3.10	LG	YG	4	CL	DRB, WG	X	I, II
12	2.630	100	10.27	2.95	CL	LBW	4	CL	G, LB		II, III
13	2.600	100	10.43	3.95	CL	LPW	4	CL	LPW		III
14	3.332	100	9.66	1.66	G	W Grey	4	G	DRB		I
15	4.685	200	10.11	5.27	LG	GBW	2	CL	WP, G		II, III

a = pH value measured after adding aqueous ammonia

b = pH value measured after passing SO₂

c = Color of solution and precipitate just after passing SO₂

d = Number of days left before precipitate and solution were separated

e = Color of solution and precipitate just before separation

Table 2.2. Chemical analysis results.

Sample Number	Experimental				Theoretical			
	Cu	SO ₃ ²⁻ †	NH ₄ ⁺	H ₂ O	Cu	SO ₃ ²⁻	NH ₄ ⁺	H ₂ O
2	46.2	41.4			49.3	41.4	0	9.3
3	39.7	37.8	4.72	17.8	40.4	38.2	4.29	17.2*
					40.6	40.9	4.61	13.8**
8	36.6	48.0	10.8	4.68	37.3	47.0	10.6	5.28
10	36.5	47.1	10.8	5.68	37.3	47.0	10.6	5.28
	2.8	2.0			3	2	0	2
3	14.3 (4.8)	10.8 (3.6)	6.0 (2.0)	22.6 (7.5)	16 5	12 4	6 2	24* 6**
8	0.96	1.0	1.0	0.44	2	2	2	1
10	0.98	1.0	1.0	0.53	2	2	2	1
2					Cu ₂ SO ₃ · CuSO ₃ · 2 H ₂ O			
3					7 Cu ₂ SO ₃ · 2 CuSO ₃ · 3 (NH ₄) ₂ SO ₃ · 2 H ₂ O* (NH ₄) ₂ (Cu(H ₂ O) ₆) [CuSO ₃] ₄ **			
8					2 Cu(NH ₄)SO ₃ · H ₂ O			
10					2 Cu(NH ₄)SO ₃ · H ₂ O			

† SO₃²⁻ Species was confirmed by MECA

CHAPTER 3

DETERMINATION OF COPPER(I) AND COPPER(II) IN MIXTURES CONTAINING BOTH SPECIES

Introduction

Aqueous solutions containing a mixture of copper(II) amines are reduced by SO_2 in the presence of an excess of NH_3 to copper(I) containing species via a series of complex reactions. Acid solutions of copper(II) are also reduced to copper(I) at the surface of copper metal in the presence of a variety of water-soluble unsaturated organic compounds that can form stable complexes with copper(I). Important information concerning the kinetics of these homogeneous and heterogeneous reactions can be obtained by the determination of the concentration of copper(I) in solution as a function of time. The continuous monitoring of either the copper(I) or copper(II) concentrations in these solutions is difficult and subject to several interferences. The reaction rates, however, can be followed by the analysis of the reaction mixture at predetermined time intervals. The concentration of copper(I) can be determined in aliquots that are withdrawn from the reaction mixture. The exclusion of copper metal from these solutions would ensure that no further conversion of copper(II) to copper(I) would occur in the course of the analysis. In a homogeneous reduction process, the reduction of copper(II) to copper(I) can be stopped for the duration of the analysis by lowering the pH of the solution or by a relatively fast determination method.

Under the conditions in which many of the kinetic studies are carried out, the rate of formation of copper(I) is slow, and during the initial stages of the reaction, the ratio of copper(II) to copper(I) in solution is large. The analytical method should, therefore, be capable of determining a low concentration of copper(I) in the presence of a relatively large concentration of copper(II). In a kinetic study it should be possible to analyze a large number of samples, preferably by means of a simple and rapid method. Additional considerations are that the analytical method should be free of interferences that are caused by the presence of an excess of complexing ligands or reducing agents.

Most of the methods that have been reported for the determination of copper(I) or copper(II) in aqueous mixture are based on redox reactions, e.g. iodometry. For example, Kiss (32) determined copper(I) and copper(II) by adding to the mixture a solution of potassium tartrate and I_2 . The I_2 oxidizes Cu(I) and in the presence of tartrate, a Cu(II) tartrate is formed. The excess I_2 is back-titrated with thiosulfate in a neutral solution. The concentration of Cu(I) in the mixture is determined from the concentration of I_2 that reacted. The Cu(II) tartrate is disrupted by a mineral acid and the total Cu content is determined by the titration of I_2 which is liberated by the reaction of Cu(II) and I^- ; the difference between the total copper concentration and the Cu(I) concentration represents the Cu(II) concentration that was present in the mixture. This method cannot be used in the presence of an excess of reducing agent. The copper(II) ion selective electrode

that is routinely employed for the determination of Cu(II) in aqueous solutions has a high sensitivity. Although solutions containing approximately 10^{-6} M copper(II) can be determined, the copper(II) ion selective electrode behaves anomalously in the presence of ligands that form complexes with copper(I) (33). The electrode response varies between 59 mv and 29 mv when the copper(II) concentration changes by a power of ten, and the response depends in a complicated manner on the type of ligand present as well as its concentration.

Electron spin resonance (ESR) spectroscopy has been used to determine Cu(II) (34). Since Cu(I) has no unpaired electrons, it appears to be a feasible method for the determination of copper(II) in the presence of copper(I).

Good reproducibility was obtained by using a capillary tube as the sample container, but the detection limit was only about 10^{-3} M. When a standard aqueous solution sample cell made of quartz was used, the detection limit was reduced to 10^{-4} M, but the reproducibility was poor. The results obtained by the ESR method will be presented later in this chapter.

The chelating agent, 2,9-dimethyl-1,10-phenanthroline (neocuproine) has been used to determine Cu(II) by first adding an excess of a reducing agent to reduce Cu(II) to Cu(I) and then, forming the colored complex, $\text{Cu}(\text{neocuproine})_2^+$ by the addition of an excess of the chelating agent. The spectrophotometric determination of copper(II) by this method has a good sensitivity ($<10^{-5}$ M), and is

relatively simple and free of interferences. This method can also be used for the determination of copper(I) in the presence of copper(II). This method should, therefore, prove useful for monitoring the formation of copper(I) in a kinetic study involving the reduction of copper(II) to copper(I). The presence of an excess of the reducing agent, in this case SO_2 , was found to interfere with the method. The use of a mixture of two complexing agents, EDTA to complex copper(II) and neocuproine to complex copper(I), gave some unexpected results that will be described later in this chapter.

Experimental

Nitrogen gas from a nitrogen cylinder is passed through an alkaline pyrogallol solution to remove traces of oxygen. Dissolved oxygen in a solution of EDTA and in a solution containing a mixture of copper(I) and copper(II), is removed by passing the purified nitrogen gas through the solution for 20–30 minutes. Two burets are filled with the two solutions under nitrogen. A predetermined volume of the copper mixture is added to an oxygen-free buffer solution in a titration vessel and the copper(II) is titrated with the EDTA solution; provision is made for measuring the pH of the solution in the titration vessel. The titration is carried out in a nitrogen atmosphere.

Reagents

Allyl alcohol and 2,9-dimethyl-1,10-phenanthroline (Aldrich Chemical Co.) were used without further purification. Reagent grade 95 percent ethanol was purified by fractional distillation of a mixture of

the ethanol, NaOH, and aluminum metal to remove any aldehydes present in the ethanol. Granular copper metal (c.p., 20–30 mesh, J.T. Baker Chemical Co.) and all other compounds were of reagent grade purity.

Preparation of Standard Solutions

A standard solution of copper(II) was obtained by dissolving copper metal in a 1:1 HNO_3 solution. A 70 percent HClO_4 solution was added and the resulting mixture heated until no more fumes from the oxides of nitrogen were evolved. The solution was diluted with distilled water to give a standard stock solution of copper(II).

Solutions containing known concentrations of copper(II) were also prepared from $\text{Cu}(\text{ClO}_4)_2$ (G.F. Smith Chemical Co.) dissolved in distilled water and standardized with EDTA, between pH 7 and 8, with murexide as indicator (35).

A standard solution of copper(I) was prepared by the complete reduction of a solution containing a known concentration of copper(II). A 10 percent solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ was added in excess to a solution of copper(II) maintained at a pH between 5 and 6 with an acetate buffer. A series of standard solutions of copper(I) was prepared in this manner and used to obtain a calibration curve (absorbance vs. concentration) for the neocuproine–copper(I) complex.

Standard solutions containing copper(I) may also be prepared by dissolving solid copper(I) chloride in a solution of neocuproine in ethanol. The copper(I) concentration in the solution can be calculated from the absorbance of the solution at 450 nm and the molar absorptivity of the copper(I)–neocuproine complex.

Mixtures containing copper(I) and copper(II) were obtained by the partial reduction of a solution of copper(II) with a deficiency of $\text{NH}_2\text{OH}\cdot\text{HCl}$. A solution of NH_3 was added to adjust the pH value of the solution to about 5. Copper(II) precipitates at pH values greater than five. The solutions were stored for several hours or even overnight to ensure that all the reducing reagent had reacted. The presence of reacted reducing reagent could cause a gradual increase in the absorbance of the solution at 450 nm due to an increase in the concentration of the copper(I)-neocuproine complexes.

Analytical Methodology and Results

Titrimetric Determination of Cu(I), Cu(II), and the Total Copper in Solution, with EDTA

Copper metal dissolved in acid was treated with a deficiency of $\text{NH}_2\text{OH}\cdot\text{HCl}$ to give mixtures containing Cu(I) and Cu(II). The total copper and the concentrations of Cu(I) and Cu(II) were determined separately as described below.

Determination of Total Copper: A measured volume of the copper mixture was transferred to the sample cell which contained 90 mL of H_2O , about 1 g NH_4Cl , and two to three drops of 30 percent H_2O_2 . After the solution had been stirred for 5 to 10 minutes, a small amount of solid murexide indicator was added and the pH value of the solution was adjusted to between 7 and 8 with dilute HCl or ammonia. The solution was titrated with EDTA until a color change from green to purple was observed at the end point.

Determination of Copper(II): The sample cell containing 90 mL H_2O ; approximately 1 g NH_4Cl , a small amount of murexide indicator, and allyl alcohol (2 M) was purged with oxygen-free nitrogen for 5 to 10 minutes. The solution containing the copper mixture was introduced into the sample cell and titrated with EDTA at pH 7 to 8 until the color of the indicator changed from green to purple.

Determination of Copper(I): After the $Cu(II)$ had been titrated, three drops of 30 percent H_2O_2 was added to the solution and stirred for 5 to 10 minutes. More murexide indicator was added and the solution was titrated at pH 7 to 8 with EDTA.

Three replicate determinations of a solution containing 0.01738 M total copper were carried out by titration with 0.01076 M EDTA. The concentration of $Cu(I)$ found was 0.005767 M and that of $Cu(II)$ was 0.01165 M with relative average deviation of less than 3 ppt.

Interferences caused by $Cu(II)$ in the determination of $Cu(I)$ were studied by Ogura et al. (36). These workers determined $Cu(II)$ and $Cu(I)$ in a system containing Cu metal, $Cu(I)$, $Cu(II)$, and allyl alcohol at equilibrium. A standard $Cu(II)$ solution was added to the $Cu(II)$, $Cu(I)$, allyl alcohol mixture and the $Cu(II)$ was redetermined. They found that there were no interferences when 0.2 M $Cu(II)$ was added to 0.1 M $Cu(I)$ in the presence of 0.1 to 1.0 M allyl alcohol.

Allyl alcohol forms complexes with $Cu(I)$ and as a consequence the oxidation of $Cu(I)$ in solution is suppressed. Purging the solution with nitrogen is nevertheless necessary to prevent oxidation. Not only should the solutions be oxygen-free, but also the atmosphere in which

the titration has to be performed should be free of oxygen. The method, therefore, is relatively slow and tedious. About 30 minutes are needed for a single determination. In the EDTA titration, copper(II) concentrations that are less than 0.01 M are difficult to determine because the end point is not sharply defined.

Spectrophotometric Determination of Copper(I) with Neocuproine

Calibration Curve. A solution containing copper(II) was reduced by an excess of $\text{NH}_2\text{OH HCl}$ between pH 5 and 6. A solution of neocuproine in ethanol was added and the mixture was maintained at an ethanol concentration of 40-50 percent (v/v) to prevent the precipitation of the Cu(I)-neocuproine complex. The solution was diluted to a specific volume and the absorbance of the solution was measured at 450 nm. A 50 percent (v/v) aqueous ethanol solution was used in the reference cell of the spectrophotometer. A typical calibration curve is shown in Figure 3.1. Absorbance of a solution at 450 nm containing 1 ppm Cu(I) in the presence of excess neocuproine is 0.122.

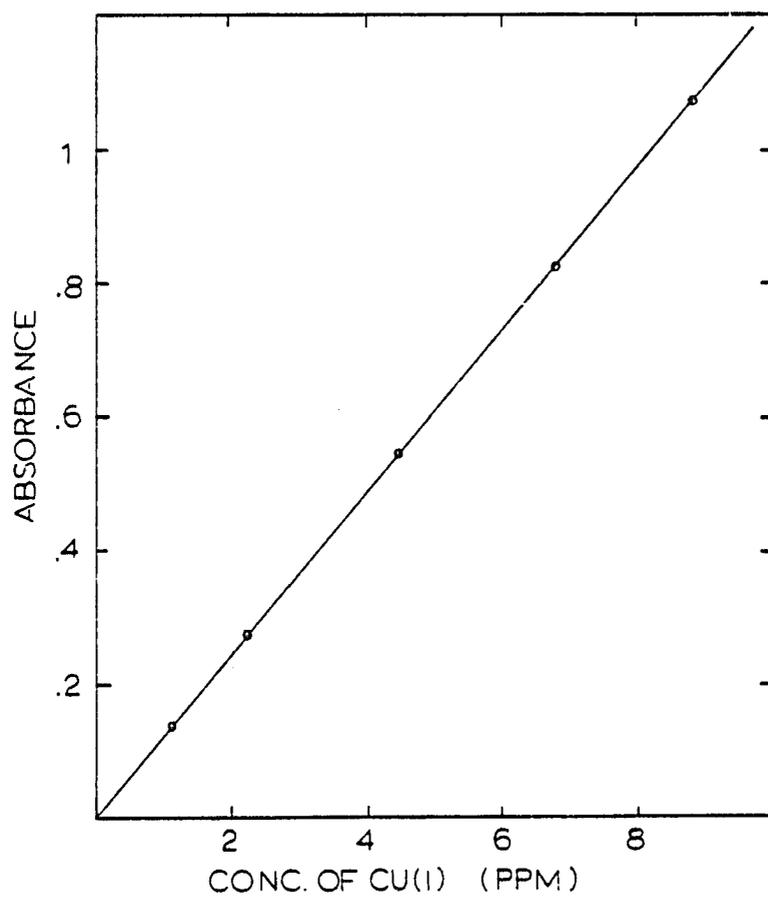


Figure 3.1. Calibration curve of Cu(I).

Factors that May Affect the Spectrophotometric Determination of the Copper(I)-Neocuproine Complex. 1) Cu(II) Ions—A large excess of copper(II) [about 100 times the concentration of copper(I)] was added to a 6×10^{-5} M solution of the Cu(I)-neocuproine complex which was formed from a mixture of Cu_2Cl_2 and neocuproine. Excess neocuproine was also added. Less than one percent difference was found in the absorbance of the resulting solution. 2) Hydrogen Ion, Allyl Alcohol and Ammonium Bisulfite—Varying concentrations of HCl and NH_3 were added to the Cu(I)-neocuproine complex obtained by the reduction of copper(II) by an excess of $\text{NH}_2\text{OH}\cdot\text{HCl}$ between pH 5 and 6 and the subsequent complexation of the copper(I) with neocuproine. In the pH range 3 to 10, the absorbance difference was one percent or less. When the pH was lower than 3, the absorbance decreased.

One to three mL of 15 percent NH_4HSO_3 and 1 to 3 mL of 99 percent allyl alcohol were added to about 50 mL of 3×10^{-5} M Cu-neocuproine complex; less than one percent difference in the absorbance was found.

Determination of Cu(I) in the Cu(I) and Cu(II) Mixture. A Cu(II) solution was mixed with a deficiency of $\text{NH}_2\text{OH}\cdot\text{HCl}$ so that partial reduction of the copper(II) occurred. Different concentrations of neocuproine were added to this solution. The absorbance values of the solution in the presence of different concentrations of neocuproine are shown in Figure 3.2. If all the Cu(II) was reduced to Cu(I), the absorbance of the solution should be 0.893. The results show that the absorbance increases as the amount of neocuproine increases after the

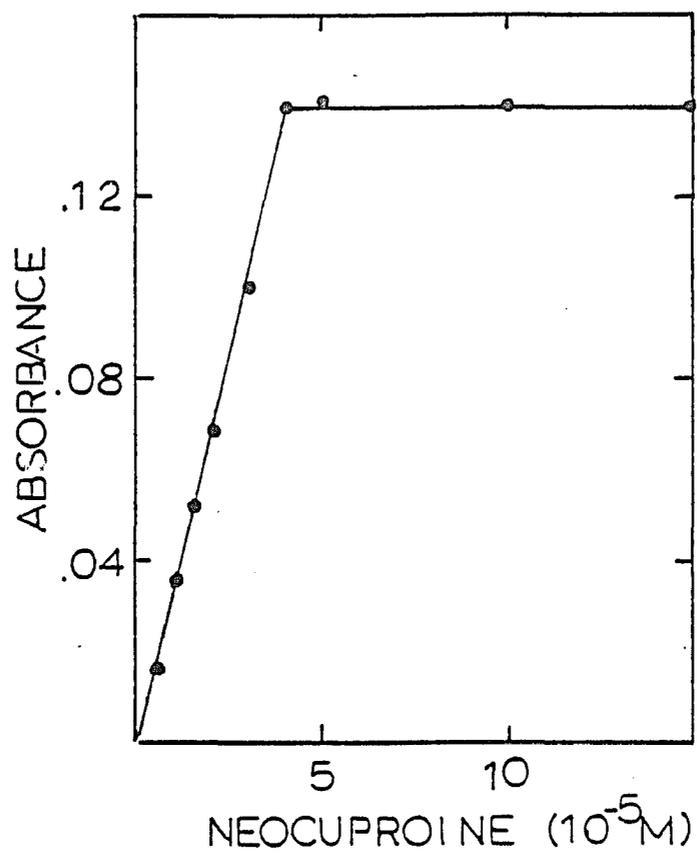


Figure 3.2. Determination of Cu(I) in a mixture of Cu(I) and Cu(II) by the addition of different amounts of neocuproine.

absorbance reached a value of 0.130, an increase in the concentration of added neocuproine has no effect. This implies that although the concentration of copper(II) is six times that of copper(I) and the concentration of neocuproine is ten times that of copper(I) the absorbance of the solution remains unchanged. It may be concluded therefore, that an excess of Cu(II) and an excess of neocuproine do not interfere with this determination.

Dissolved Oxygen. Oxygen dissolved in the solution affects the Cu(I) neocuproine complex formation. This can be shown by carrying out the following experiments.

A solution containing 10 mL of neocuproine, 30 mL of ethanol, and 50 mL H₂O was added to the Cu(I) and Cu(II) mixture. If the oxygen in this solution was removed with nitrogen gas for five minutes and then mixed with the copper solution, the absorbance of the solution at 450 nm was 0.702. If the solution was added without displacing the dissolved oxygen, the absorbance was found to have decreased to a value of 0.686. If the copper solution was mixed with oxygen-free neocuproine solution and then ethanol and water were added, the absorbance was found to be 0.848. If neocuproine and ethanol were mixed and the solution purged with nitrogen and the copper solution and water added subsequently, the absorbance was found to be 0.860. In the last instance, if oxygen-free water was used, the absorbance would increase by another 1.5 percent. In the routine studies, all the solutions were oxygen-free and water was added after the copper mixture had been mixed with neocuproine and ethanol.

Time Dependence of the Solution Absorbance. The addition of neocuproine to the copper(I)-copper(II) mixture resulted in the formation of the neocuproine-copper(I) complex in the ethanol-water solution. The absorbance of the solution, measured at different time intervals, showed a progressive increase. One example is shown in Table 3.1.

A blank solution was made by the addition of neocuproine to a solution of copper(II). The absorbance of the ethanol-water solution also showed a time dependent increase in absorbance. The results are shown in Table 3.2.

The increase in the absorbance may be due to impurities in the solution which gradually reduce Cu(II) to Cu(I). Nevertheless, the increase in the absorbance of this solution is less than two percent, if the measurements are carried out within a period of four hours.

Table 3.1. Time dependence of the sample solution absorbance.

time (hr.)	.2	1	2	3	4	6	24	48
absorbance	0.396	0.397	0.399	0.401	0.402	0.406	0.413	0.418

Table 3.2. Time dependence of the blank solution absorbance.

time (hr.)	0.3	1.5	4	6	12	25
absorbance	0.007	0.009	0.011	0.012	0.014	0.017

Spectrophotometric Determination of Copper(I) with a Mixture of EDTA and Neocuproine

The formation constant of the EDTA complex of Cu(II) is greater than the formation constant of the EDTA complex of Cu(I) by a factor of 10^{11} (37). The yellow neocuproine complex of Cu(I), $\log \beta_2 = 19.1$ (38), has an absorption maximum at 450 nm and the Cu(II) complex of neocuproine, $\log \beta_2 = 11.7$ (38), does not interfere with the spectrophotometric determination of copper(I) with neocuproine. If a mixture of neocuproine and EDTA is used to determine Cu(I), in the Cu(I) and Cu(II) mixture, neocuproine complexes with Cu(I); the EDTA which masks the Cu(II) should prevent the possible reduction of Cu(II) to Cu(I). When the mixture of 3 to 1 mole ratio of neocuproine and EDTA was used to determine Cu(I) in the Cu(I) and Cu(II) mixture, the absorbance of the solution was constant and did not change with time for a few days. It appears, therefore, that the EDTA does mask the excess Cu(II) and prevents further reduction of the Cu(II) to Cu(I). However, the absorbance of this solution containing the two ligands is always lower than the absorbance that is obtained when neocuproine alone is used. A further decrease in the absorbance was observed when the EDTA:neocuproine ratio was increased. The presence of EDTA in solution probably prevents the conversion of all the Cu(I) into the $\text{Cu}(\text{neocuproine})_2^+$ complex and thereby decreases the measured absorbance at 450 nm. The following series of experiments was designed to clarify this anomalous result. The absorbance of a solution that was 1.34×10^{-4} M in Cu(I) and 5×10^{-4} M in neocuproine was

measured at 450 nm and found to remain unchanged with time for at least 24 hours. In the presence of 0.05 M allyl alcohol, the absorbance of the solution remained unchanged for a period of 10 days. The same experiment was carried out with a solution that was 1.34×10^{-4} M in copper(I), 5.0×10^{-4} M in neocuproine, and 1.0×10^{-3} M in EDTA; the EDTA solution was added after the Cu(I)-neocuproine complex was formed. The initial absorbance of the solution at 450 nm was the same as that obtained in the previous experiment, but decreased with time until a constant absorbance value that was about 6 percent lower than the initial value was reached in about three days. If the experiment was repeated with the same initial concentrations of copper(I), neocuproine, and EDTA, the only difference being that the neocuproine and EDTA solution were added simultaneously (in the form of a mixture) to Cu(I), the initial absorbance was 20 percent lower than that obtained in all the previous experiments. The absorbance increased slowly with time, and after about two weeks approached the constant absorbance value that was obtained in the earlier experiment. The presence of 0.05 M allyl alcohol in these solutions merely decreased the time required to reach the equilibrium absorbance value. The results of these experiments led to the conclusion that neocuproine and EDTA form a mixed ligand complex with copper(I) and that the molar absorptivity of the mixed ligand complex is less than that of the Cu(I)-neocuproine complex.

EPR Determination of Copper(II)

The EPR method has been used by Guilbault et al. (34) to quantitatively determine Cu(II). If the amplitude of the Cu(II) peak is measured and plotted vs. the concentration of Cu(II), a linear calibration curve is obtained. In our studies, we were unable to position the standard quartz aqueous solution sample cell in a reproducible manner in the sample cavity. This effect is evident from the results shown in Figure 3.3. In this case, the detection limit is about 10^{-4} M Cu(II). When a capillary tube with 1 mm diameter was used, much better reproducibility was obtained, but the detection limit is about 10^{-3} M Cu(II). The calibration curve is shown in Figure 3.4. Three to nine mL of 45 percent NH_4HSO_3 mixed with 40 mL of 0.06137 M CuSO_4 and diluted with water to 50 mL were studied by EPR in the quartz aqueous cell. After inserting the cell in the sample cavity it was left there until all the measurements were completed. In this case, even though the absolute concentration of Cu(II) was not determined, the relative change in the concentration of Cu(II) was obtained. It was found that, in 10 to 30 minutes after Cu(II) and NH_4HSO_3 were mixed, the rate of decrease of the copper(II) was proportional to the concentration of NH_4HSO_3 added. The results are plotted in Figure 3.5.

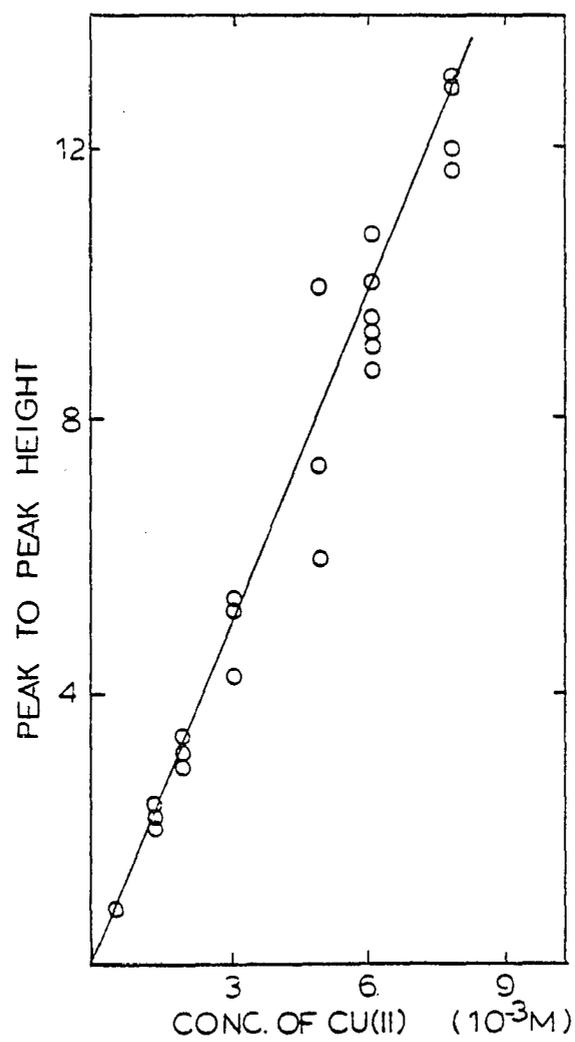


Figure 3.3 EPR determination of Cu(II) using a quartz cell.

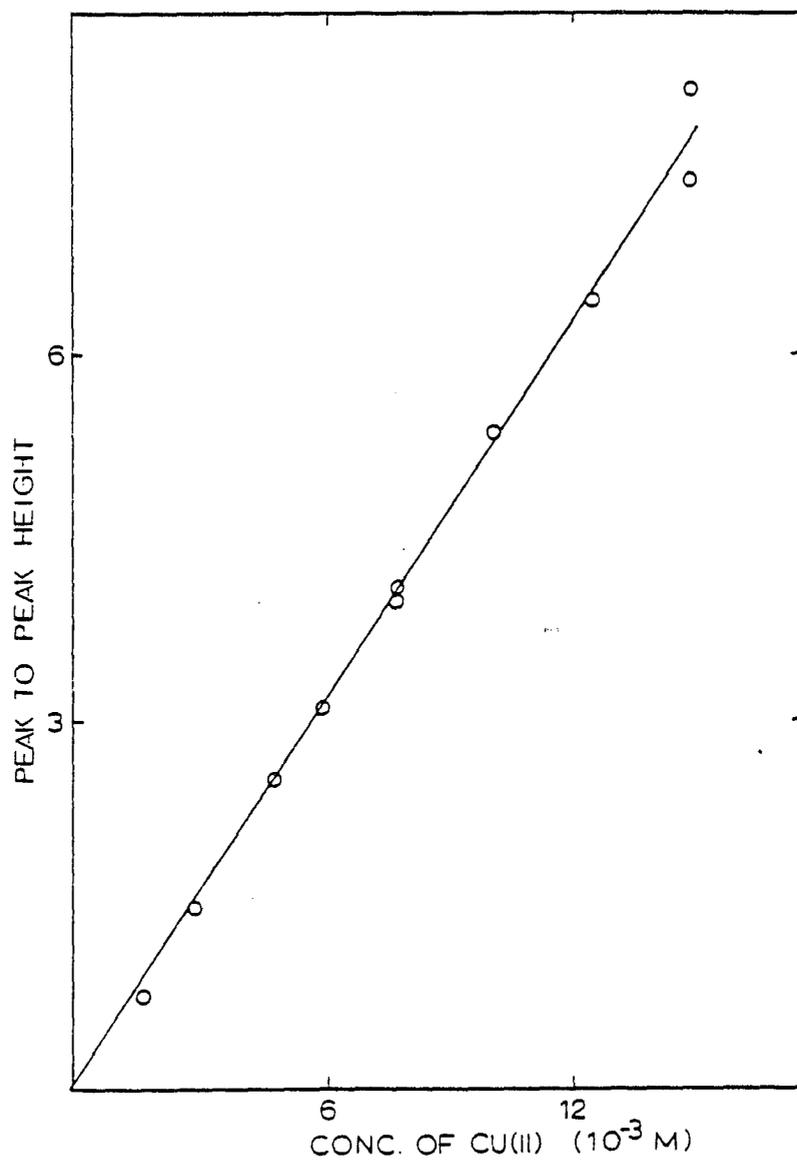


Figure 3.4. EPR determination of Cu(II) using a capillary tube.

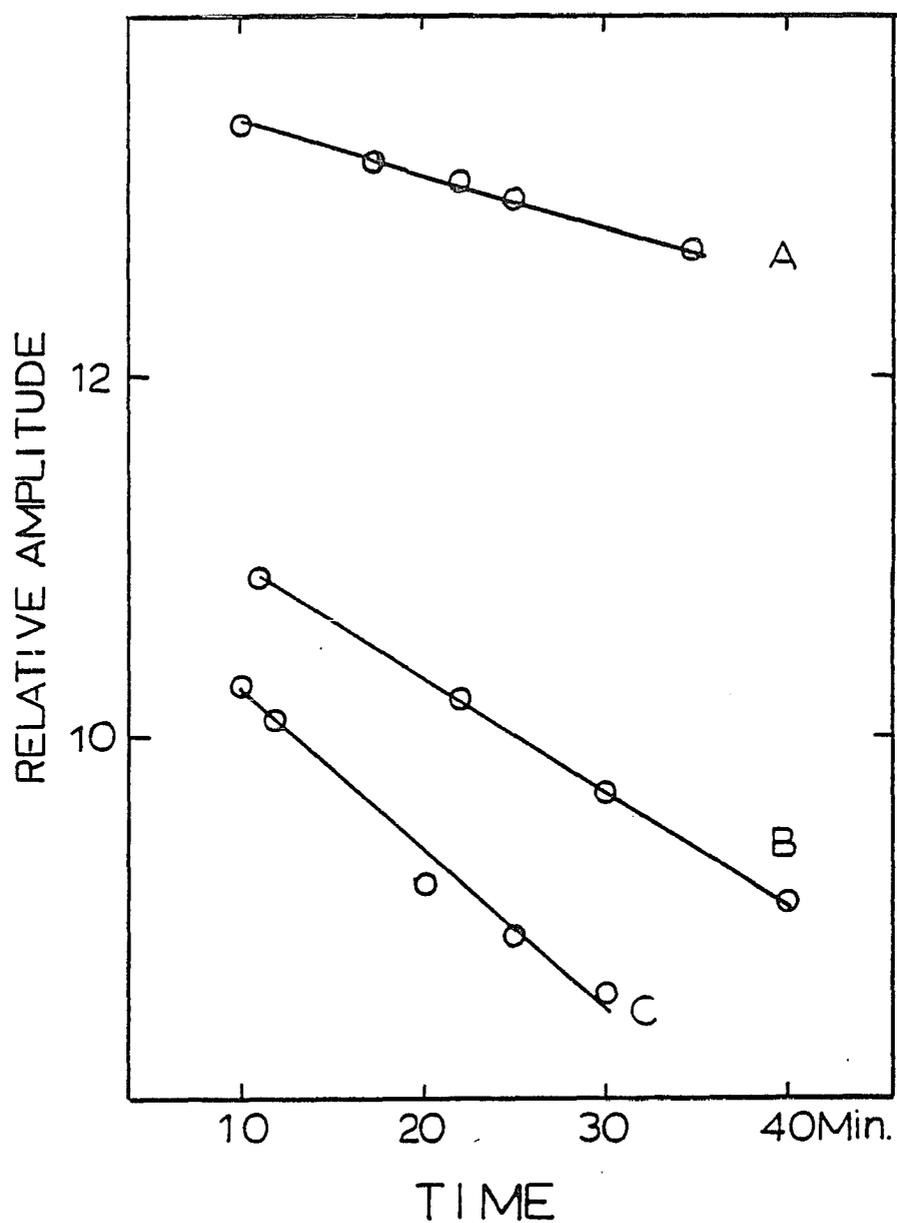


Figure 3.5. EPR determination of the change in Cu(II) as a function of time. (A) 3 mL of NH_4HSO_3 and 40 mL of CuSO_4 diluted to 50 mL (B) 6 mL of NH_4HSO_3 and 40 mL of CuSO_4 diluted to 50 mL (C) 9 mL of NH_4HSO_3 and 40 mL of CuSO_4 diluted to 50 mL. Concentration of CuSO_4 is 6.14×10^{-2} M, NH_4HSO_3 is 45 percent in aqueous solution.

Determination of Cu(I) and Cu(II) with EDTA in a Reaction Mixture
Containing Cu(II), Elemental Copper and Allyl Alcohol

A solution containing 4.6 g of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 12 mL of 70 percent HClO_4 , 34 mL of allyl alcohol was mixed with sufficient water and made up to a total volume of 1 L. This solution contained 0.01204 M Cu(II) and 0.5 M allyl alcohol and the pH of the solution was 1.2. Four-hundred mL of this solution was purged with nitrogen gas for 12 minutes and was left in the sample cell. A 170 cm copper wire was introduced into the cell. After one day, 10 mL of this solution was withdrawn and Cu(II) and total copper were determined by EDTA. The copper(I) concentration was obtained from the difference between the total copper and Cu(II). The results are plotted in Figure 3.6. The ratio of the slopes of the copper(I) curve and the total copper curve is 1.8:1, the expected value being 2:1. The concentration of the Cu(I) and Cu(II) approached constant values after about 70 hours and the calculated value of the equilibrium constant, $K = [\text{CuL}_2^+]^2 [\text{CuL}_2^{2+}]^{-1}$ was 158, where L represents allyl alcohol. The total amount of Cu(I) and Cu(II) that is greater than twice the initial concentration of Cu(II), i.e., 24×10^{-3} M, suggested that some of the Cu(I) that was formed was oxidized in the presence of oxygen to Cu(II) which could react further with copper metal to produce an additional amount of Cu(I). This also caused the ratio of the slopes of the two curves to be somewhat less than 2. Extrapolation of the curves in Figure 3.6 indicated that Cu(I) started to form after 11 hours. This may be misleading because the presence of oxygen in these solutions can result in the oxidation of copper(I) that is formed initially.

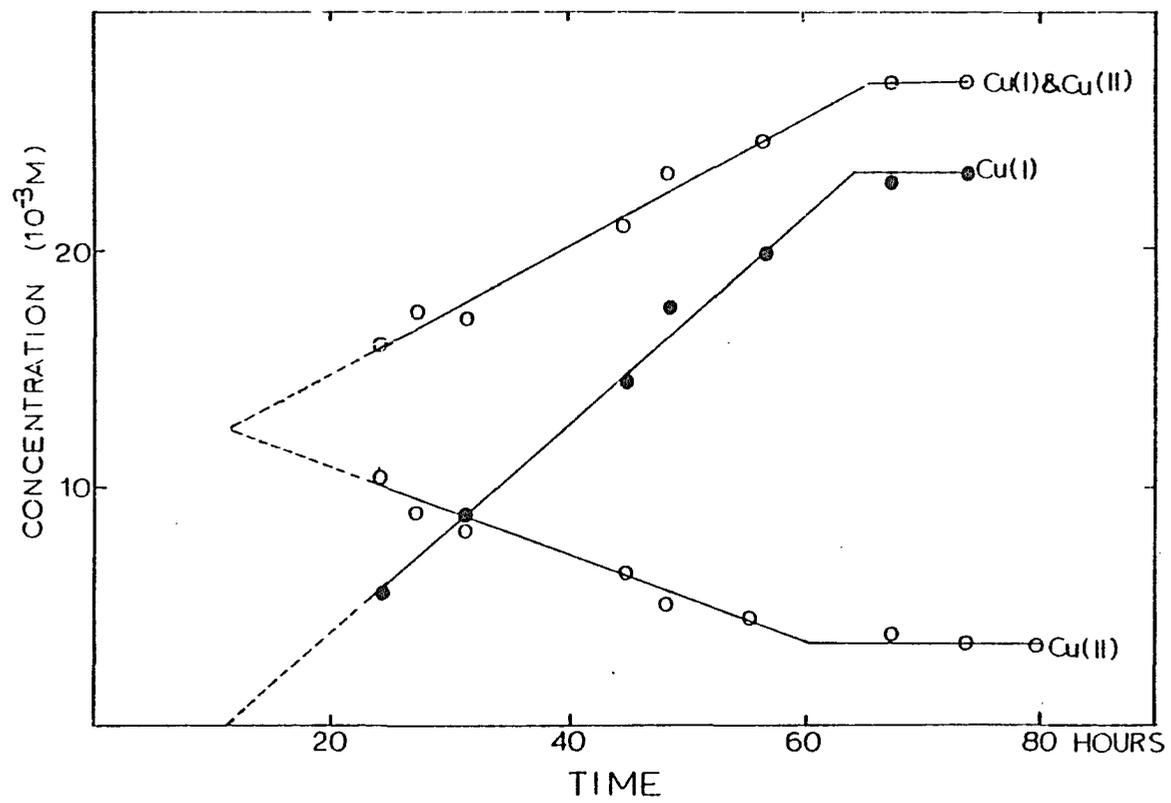


Figure 3.6. Determination of Cu(I) and Cu(II) with EDTA.

Discussion

The use of a mixture of EDTA and neocuproine gave unexpected results. This method could not be used for the determination of copper(I) in the presence of SO_2 . The use of neocuproine, however, appears to be a simple and rapid method for the determination of Cu(I) in the course of the reduction of Cu(II) by copper metal in the presence of allyl alcohol. The EDTA method is tedious and less accurate and it is not suitable for the kinetic studies. It is not possible to prepare standard solutions containing known concentrations of Cu(I) and Cu(II). The accuracy of the spectrophotometric method cannot, therefore, be directly verified.

The interferences caused by oxygen are difficult to avoid in the EDTA titration. This was shown previously in this chapter. It is possible that the copper(I)-allyl alcohol forms an addition complex with oxygen (39). This would explain the difficulty that is encountered in removing the last trace of oxygen from these solutions. It is also possible that a mixed ligand complex of copper(I), EDTA and neocuproine is present in solution. It has been reported that the color of the $\text{Cu}(\text{neocuproine})_2^+$ complex developed slowly and incompletely in the presence of EDTA (40). Recently, ternary complexes containing copper(I), neocuproine, and ligands containing oxygen donor atoms such as acetylacetone, acetate, and oxalate ions have been synthesized by Kwik et al. (41). They also found the molar absorptivity of these compounds at 450 nm were between 3000 to 4000 $\text{cm}^{-1} \text{M}^{-1}$ which is much lower than the value of 7700 $\text{cm}^{-1} \text{M}^{-1}$ which is obtained for the $\text{Cu}(\text{I})(\text{neocuproine})_2$ complex.

In this work the following compounds of Cu(I), neocuproine and EDTA has been postulated. Attempts should be made in the future to synthesize such compounds and investigate their properties. Determination of the molar absorptivity of the Cu(I).(neocuproine).(EDTA) complex either directly or indirectly, should help to evaluate the anomalies that have been observed in the spectrophotometric methodology.

The EPR method for the determination of Cu(II) in the presence of Cu(I) is still a promising method. Because the position of the sample cell cannot be controlled in an exact manner, the sample cell should be fixed in the microwave cavity and the solution introduced into the cell without moving the cell. If reproducible results are obtained by the EPR method for Cu(II) determinations, a comparison of the results obtained by the EPR method and the neocuproine method should be carried out. If successful, the EPR method should be used to monitor changes in the Cu(II) concentration in the kinetic studies involving the reduction of ammoniacal solution of Cu(II) with SO₂.

CHAPTER 4

DETERMINATION OF SULFUR DIOXIDE WITH A MIXTURE OF NEOCUPROINE AND COPPER(II)

Introduction

Sulfur dioxide is a colorless gas with a pungent, irritating odor. Its odor can be detected when it is present in concentrations of 0.3 to 1 ppm (780 to 2620 $\mu\text{g}/\text{m}^3$). It is one of the major atmospheric pollutants. Its worldwide emission has been estimated at 146 megatons/year by Robinson and Robbins (42) and as 100 megatons per year by Kellogg et al. (43), who predict emissions of about 275 megatons per year for the year of 2000. Cavender et al. (44) estimated that the emission of sulfur dioxide from the U.S. for 1970 was 33.9 megatons. Power plant and industrial emissions accounted for 70 percent and 18 percent respectively. Intensive efforts are being made to control sulfur dioxide by either removing sulfur from coal and oil or removing sulfur dioxide at the combustion source (45).

There are many methods for SO_2 determinations (46). One of the most popular methods was developed by West and Gaeke (47). In this method, SO_2 was absorbed in a solution of potassium tetrachloromercurate (TCM) to form a dichlorosulfitomercurate complex (DCSM) which resists oxidation by either the oxygen in the air or that dissolved in the absorbing solution. The spectrophotometric determination of SO_2 is based upon the measurement of the red-violet

color produced by the reaction of DCSM with hydrochloric acid, pararosaniline, and formaldehyde. The intensely colored pararosaniline methyl sulfonic acid with a molar absorptivity of 4.77×10^4 acts as a two-color pH indicator. The pH of the final solution may be adjusted to 1.6 ± 0.1 by addition of 3 M phosphoric acid and the absorbance of the solution is read at 548 nm. When the final pH was controlled at 1.2 ± 0.1 . The molar absorptivity is 3.70×10^4 at 575 nm (48). Since each mole of the colored aldehyde addition product contains three moles of SO_2 , the molar absorptivity of the addition product per mole of SO_2 is equivalent to a value between 12×10^3 and 16×10^3 . Stephens et al. (49) determined SO_2 by using a mixture of Fe(III) and 1,10-phenanthroline. Fe(III) is reduced by SO_2 to Fe(II) which formed a colored complex with 1,10-phenanthroline. Since one mole of SO_2 can reduce two moles of Fe(III) and forms 2 moles of $\text{Fe}(1,10\text{-phenanthroline})_3^{++}$ complex with a molar absorptivity of 11,100; the molar absorptivity of the complex is equivalent to a value of 22×10^3 per mole of SO_2 which is even better than that obtained by the pararosaniline method. However, it was found that the reaction was temperature dependent and a thermostat was necessary for quantitative analysis. Attari et al. (50) elucidated the stoichiometry of the reaction between Fe(III) and SO_2 in an acetate solution at various temperatures. They found that dithionate, $\text{S}_2\text{O}_6^{2-}$, was formed at temperatures below 25°C and sulfate was formed at temperatures higher than 40°C , a mixture of dithionate and sulfate was formed.

Neocuproine forms a complex with Cu(I). The molar absorptivity of $\text{Cu}(\text{neocuproine})_2^+$ is 7,700 at 450 nm in 1:1 ethanol aqueous solution. Again, the reaction between Cu(II) and SO_2 is suspected to be 2:1 reaction. Therefore, the molar absorptivity of the complex is equivalent to 14×10^3 per mole of SO_2 which is comparable with that obtained by the two previous methods. The method appears to be simple and the possibility of using Cu(II) and neocuproine for the determination of SO_2 investigated and the results are reported below.

Experimental

Equipment

Sulfur dioxide was obtained by diffusion from sulfur dioxide permeation tube which was maintained at 30°C . The SO_2 gas was swept out by air or by an inert gas, such as nitrogen.

The permeation tubes were obtained from Analytical Instrument Development, Inc., PA. They were calibrated by weighing them before and after they were in use for different periods of time.

An Orion Research pH meter model 811, for the pH measurements and a Perkin Elmer 552 spectrophotometer was used for absorbance measurements.

A 25 mL gas scrubber bottle was used as the solution container in the gas absorption experiments.

A calibrated flow meter which was constructed in the laboratory was used to measure gas flow rates.

Whenever temperature control was needed, a water bath was used, and the temperature was controlled with the aid of a thermostat. In all other experiments the temperature was controlled within $\pm 1^{\circ}$.

Chemicals

Neocuproine with a purity of 99 percent from Aldrich Chemical Co., and reagent grade $\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$, NaH_2PO_4 , Na_2HPO_4 , NaOAc , HOAc , NaOH , HCl , 95 percent ethanol, H_3PO_4 , and disodium salt of EDTA, were used in this work.

General Procedure

A carrier gas (air or nitrogen) swept sulfur dioxide from a permeation tube through 25 mL of a mixture of Cu(II) neocuproine, which was in 40–50 percent of an aqueous–ethanol solution, for a predetermined period of time. The flow rate of the gas was controlled to 50 ± 10 mL/min. One mL of 0.01 M EDTA was then added to the resultant solution and stirred thoroughly. The absorbance of the solution was then measured at 450 nm, with a 1:1 ethanol: H_2O mixture in the reference cell.

Factors that Affect the Spectrophotometric Method

Slow Kinetics

The absorbance of the sample solution that contained copper(I), copper(II), and neocuproine, and blank solution containing copper(II) and neocuproine increased slowly with time at 450 nm. If EDTA is added to these solutions, however, the absorbance values of the solutions remain constant. In order to obtain constant absorbance values for the

sample and blank solutions, the EDTA was added after the blank solution was stored for a specific time and after the SO_2 was passed through the sample solution. The absorbance of the sample solution decreased gradually at the beginning, but remained constant after several days had elapsed. This decrease in the absorbance was attributed to the formation of a mixed ligand complex of Cu(II) as described in the last chapter.

A series of solutions which contained 2 mL of $5 \times 10^{-3}\text{M}$ $\text{Cu}(\text{ClO}_4)_2$ and 4 mL of $5 \times 10^{-3}\text{M}$ neocuproine were diluted with the mixture of ethanol and water to 25 mL. Sulfur dioxide ($8 \mu\text{g}/\text{min}$) was passed through these solutions for 15 minutes. One mL of 0.01 M EDTA solution was added to each solution and the absorbance was measured at different times after the EDTA was added. The results are shown in Table 4.1 and are plotted in Figure 4.1. It was found that the absorbance value is constant after two hours. In later studies, absorbance values were measured after this period of time had elapsed.

Table 4.1. The effect of time on the absorbance of a solution containing copper(I), copper(II), and neocuproine, after the addition of EDTA.

No.	Time Delay (min)	Abs.	Time Delay (hr)	Abs.	Abs. After			
					10-12 hr	22-24 hr	30-32 hr	100 hr
1	75	.239	4.3	.227	.226	.227		
2	60	.248	4.0	.231	.233	.232	.230	.232
3	45	.258	3.8	.232	.231	.232	.230	.231
4	30	.260	3.5	.231	.232	.231	.230	.230
5	15	.263	3.3	.228	.227	.226	.226	.227

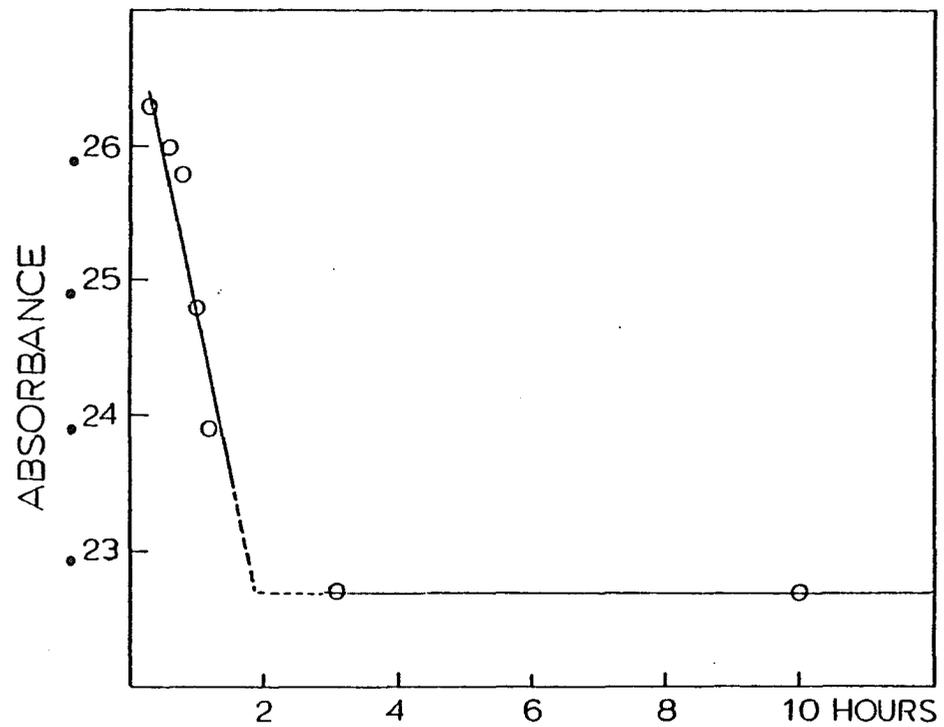


Figure 4.1. The effect of time, after the addition of EDTA, on the absorbance of a solution containing Cu(II), SO₂ and neocuproine.

The Concentration of Neocuproine and Initial pH of Solution

The procedure used was the same as described above. The volume of neocuproine that was added to the $\text{Cu}(\text{ClO}_4)_2$ solution was varied from 2 to 10 mL. The results are plotted in Figure 4.2. When 4 mL of 5×10^{-3} M neocuproine was added, a maximum absorbance was obtained. For the following studies, $\text{Cu}(\text{ClO}_4)_2$ and neocuproine in a molar ratio of 1:2 were used. The initial pH value of the solution of neocuproine and $\text{Cu}(\text{ClO}_4)_2$ was varied from 3 to 10 by adding 0.1 M HCl and 0.1 M NaOH. The absorbance value of the solution vs. the initial pH value of the solution is plotted in Figure 4.3. There was a gradual increase of absorbance from pH 3 to pH 6. Between pH 7.2 to 8.4 the absorbance approaches a maximum; the absorbance decreased again at pH above 9. A buffer solution containing NaH_2PO_4 and Na_2HPO_4 was used to maintain the pH of the solution at 8.2 in order to obtain a maximum absorbance, but a precipitate of $\text{Cu}(\text{OH})_2$ was formed in about half an hour after the solution was buffered.

Calibration Curve and Blank

Sulfur dioxide, (8 $\mu\text{g}/\text{min}$) was passed through a mixture of 25 mL of ethanol-water solution which contained 2 mL of 5.0×10^{-3} M $\text{Cu}(\text{ClO}_4)_2$ and 4 mL of 5×10^{-3} M neocuproine, for different periods of time. The initial pH of the solution was 5.5 and no buffer was employed. A second gas scrubber containing the same solution was connected in series with the first scrubber. The absorbance of the solution in the second scrubber was the same as the blank even after SO_2 had been passed for 70 minutes. Hence, SO_2 was considered to

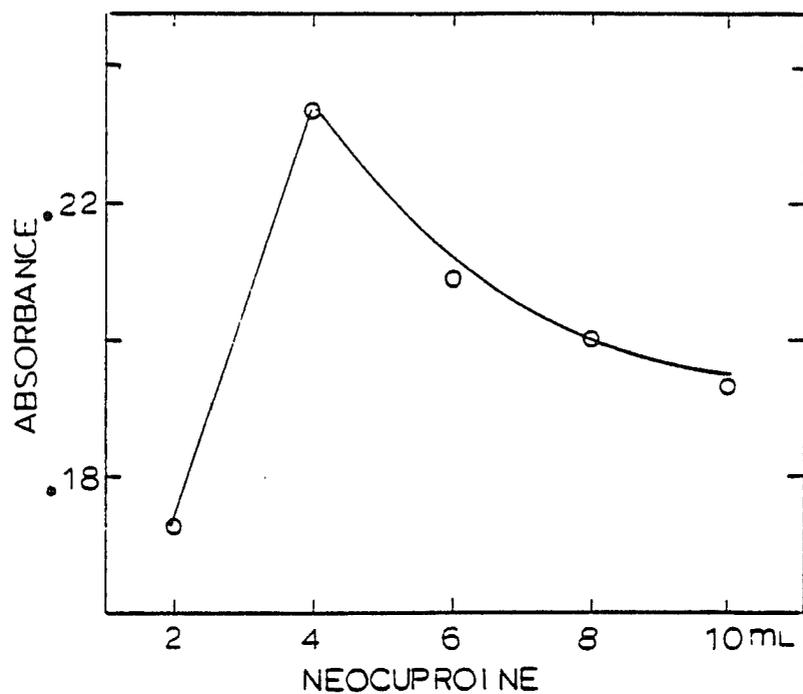


Figure 4.2. The effect of volume of 5×10^{-3} M neocuproine on the absorbance of a 25 mL of solution containing 2 mL of 5×10^{-3} M $\text{Cu}(\text{ClO}_4)_2$ and 120 μg of SO_2 . EDTA was added after SO_2 was absorbed.

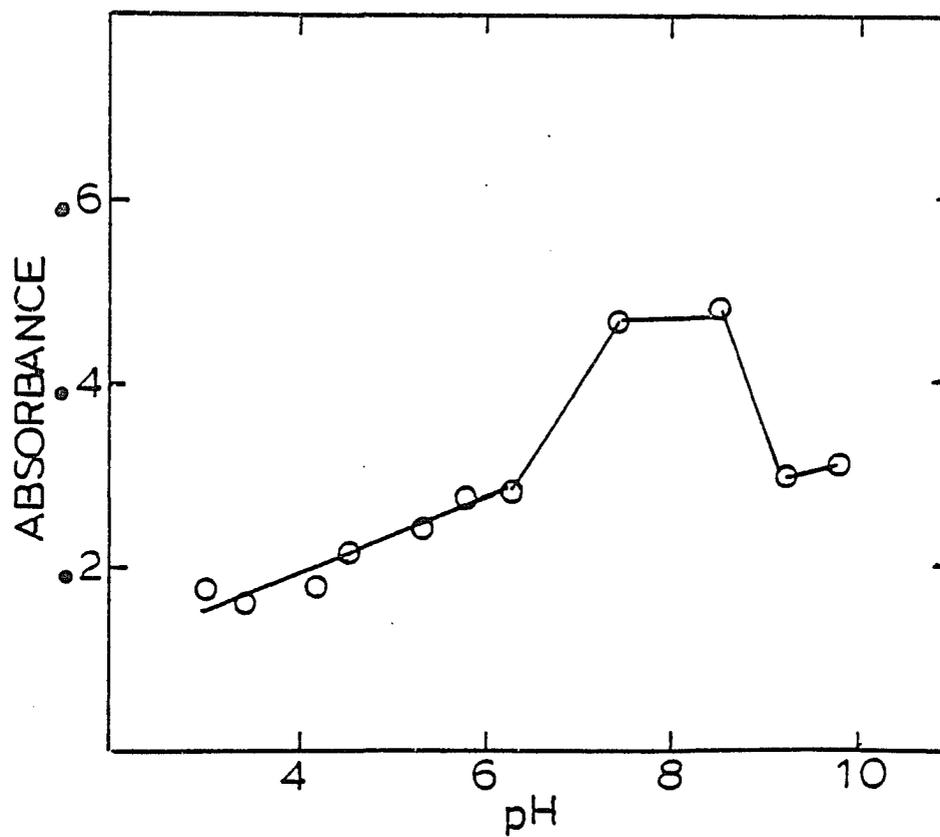


Figure 4.3. The effect of initial pH on the absorbance of a solution containing Cu(II), neocuproine and SO₂. EDTA was added after SO₂ was absorbed.

be completely absorbed in the first gas scrubber when the gas was passed through this solution for as long as 70 minutes. After the SO_2 was passed through the solution, 1 mL of 0.01 M EDTA was added to the solution. The absorbance of the solution at 450 nm was measured after the addition of the EDTA solution and after the mixture was allowed to stand for at least three hours.

The results are shown in Figure 4.4. It was found that the absorbance increased as expected, when the SO_2 was passed through the solution for varying periods of time up to 15 min; beyond this the absorbance of the solution showed an unexpected decrease as shown in Figure 4.4.

When an acetate buffer was added to control the pH at 6.2, and the above experiment repeated, the increase in absorbance versus the amount of SO_2 absorbed is shown in Figure 4.5. In this case, the absorbance did increase with increasing amount of SO_2 absorbed.

To a blank solution buffered as before, was added 0.01 M EDTA after the blank was allowed to stand for different periods of time. The longer the blank solution was allowed to stand, the higher its absorbance. The results obtained are shown in Figure 4.6.

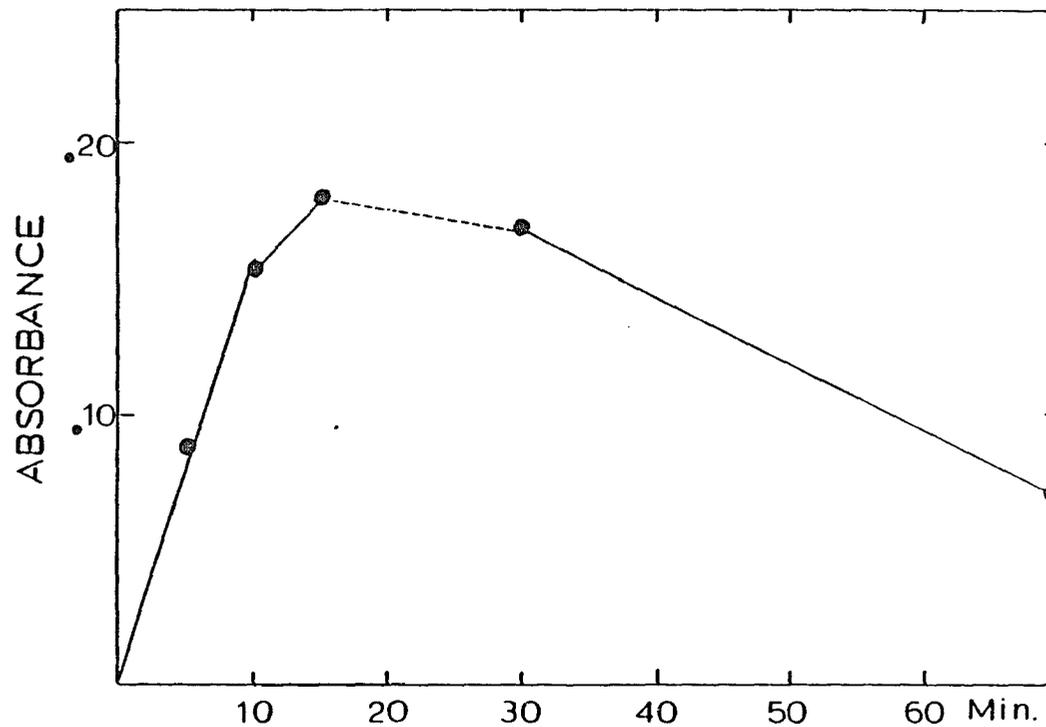


Figure 4.4. Calibration curve for SO_2 in the absence of a buffer. The solution contained Cu(II) , neocuproine and SO_2 . EDTA was added after SO_2 was absorbed. The amount of SO_2 was varied by passing the gas through the solution for different periods of time.

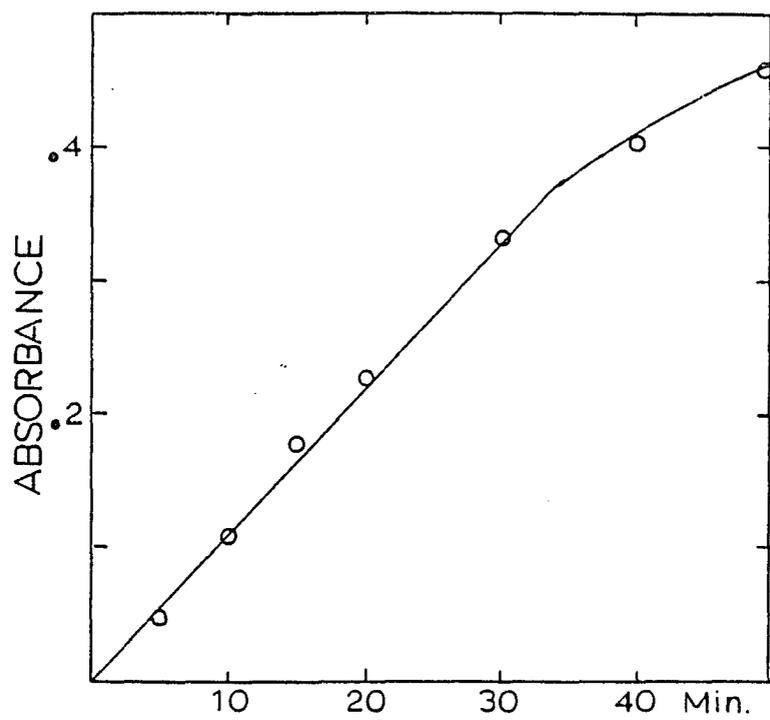


Figure 4.5. Calibration curve for SO₂ in the presence of an acetate buffer. The amount of SO₂ was varied by passing SO₂ gas for different time periods. The flow rate of SO₂ is 8 µg/min.

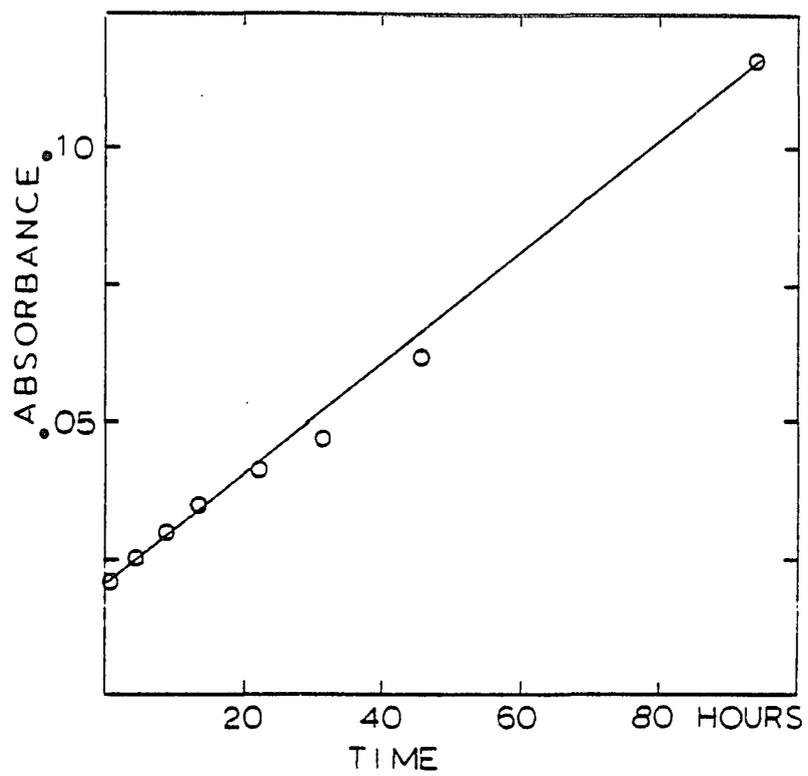


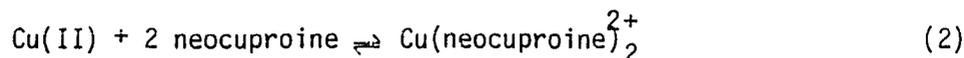
Figure 4.6. Increase in absorbance of the blank with time before EDTA was added.

Discussion

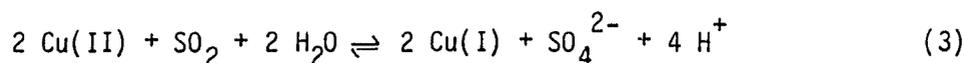
Cu(I) reacts with neocuproine and forms an orange-yellow complex as shown in equation 1.



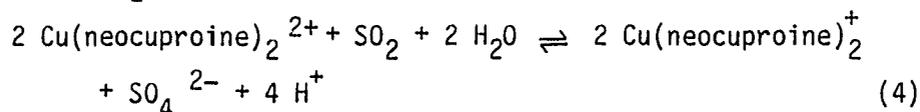
The formation constant for $\text{Cu(neocuproine)}_2^+$ is about 10^{19} . Cu(II) also forms a complex with neocuproine; however, its formation constant is only 10^6 . The reaction is shown in equation 2.



When SO_2 is passed through a mixture of Cu(II) and neocuproine, the Cu(II) is reduced to Cu(I) (equation 3).



It is also possible that SO_2 reduces $\text{Cu(neocuproine)}_2^{2+}$ to $\text{Cu(neocuproine)}_2^+$ (equation 4).



EDTA (H_4Y), was added to the reaction mixture, after passing SO_2 , in order to complex the unreacted Cu(II) as shown in equation 5.

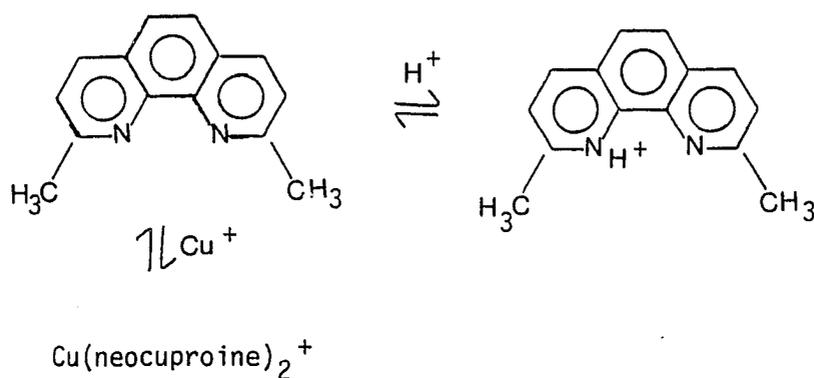


However, EDTA may also compete with neocuproine to form a mixed ligand complex.

When the Cu(II) concentration was kept constant and the concentration of neocuproine was varied it was found that the optimum concentration of neocuproine was twice that of Cu(II). This seems reasonable since Cu(I) reacts with neocuproine in a 1:2 mole ratio. An excess of neocuproine favors the formation of the copper(II)-neocuproine complex and decreases the concentration of uncomplexed Cu(II) and

thereby decreases the concentration of the Cu(I)-neocuproine complex that can be formed by SO_2 reduction.

The pH of the solution plays an important part in this determination of SO_2 . Higher pH values not only favor the reduction of Cu(II) to Cu(I) (equations 3 and 4), but also favor the formation of the $\text{Cu}(\text{neocuproine})_2^+$ complex as shown below.



When the solution is not buffered, the SO_2 added eventually decreased the pH of the solution. This change in pH versus increase in the concentration of SO_2 is shown in Figure 4.7. From Figure 4.3 it is evident that low absorbance values are obtained at low pH values. The calibration curve, however, in Figure 4.4 which showed a decrease in the absorbance is anomalous. Several experiments were conducted in order to clarify this problem. Experiments were repeated in unbuffered solutions and no EDTA was added to the solution after the SO_2 reduction was carried out. The calibration curve obtained is shown in Figure 4.8. No increase in the absorbance of the solution was observed after the SO_2 gas was passed through the solution for 15 minutes.

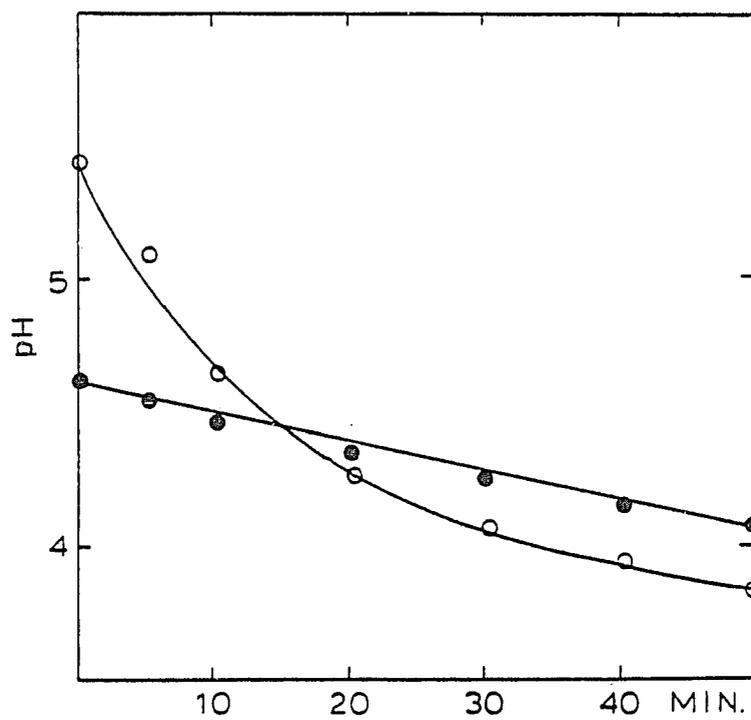


Figure 4.7. Changes in pH as a function of SO₂ gas absorbed by solution. Time represents the time during which SO₂ was passed through solution.

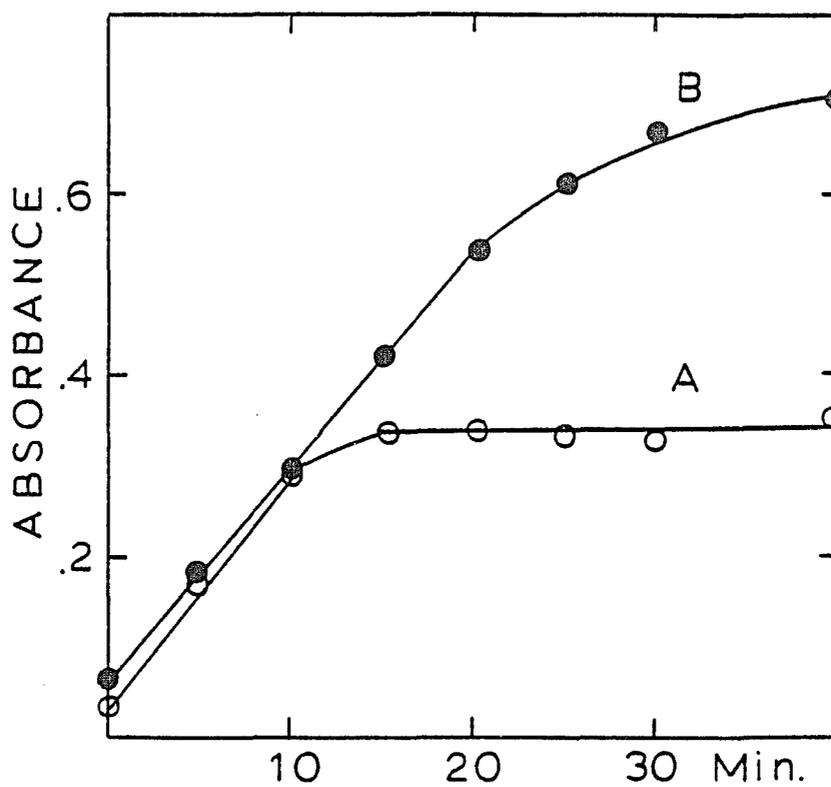


Figure 4.8. Calibration curve for SO_2 without the addition of EDTA. The solution absorbance was measured at different time intervals. (A) measured in 3 hours (B) measured after 20 hours. The time on the abscissa represents the time during which SO_2 was passed through the solution.

The absorbance increased after standing for 20 hours. It is conceivable that other sulfur containing anions were formed in this period of time which gradually reduced Cu(II) to Cu(I). In the presence of EDTA, the stable complex, CuY^{2-} is formed and stopped the relatively slow reduction process. The decreasing absorbance may be caused by the formation of a higher concentration of the Cu(I) mixed ligand complex at low pH. The possible disruption of the Cu(I)-neocuproine complex by SO_2 was also examined between pH 5 and pH 3.75, but no such effect was observed.

It seems feasible from this work, to use the buffered Cu(II)-neocuproine solution to determine SO_2 in gas samples. A sample of gas containing SO_2 can be passed through the solution for as long as several days, and the corrected absorbance of the solution can be used to determine the concentration of SO_2 in the gas sample. The Cu(I)-neocuproine complex may also be extracted from the 1:1 ethanol-water solution into 1,2-dichloroethane in order to increase the sensitivity of the determination. When the concentration of $\text{Cu(I)(neocuproine)}_2$ was calculated, however, it was found that the efficiency was only 10 to 20 percent. When nitrogen was used as carrier gas instead of air, the efficiency was found to be better than 85 percent. Not only did the reducing efficiency increase, but also, the phenomenon of slow kinetics disappeared. A linear calibration curve was obtained even after passing the SO_2 ($6.4 \mu\text{g SO}_2/\text{min}$) for 25 minutes (Figure 4.9). It was assumed that the oxygen in the air not only reoxidized Cu(I) back to Cu(II), but also participated in the formation of the sulfur compounds which was involved in the slow reduction of Cu(II) to Cu(I).

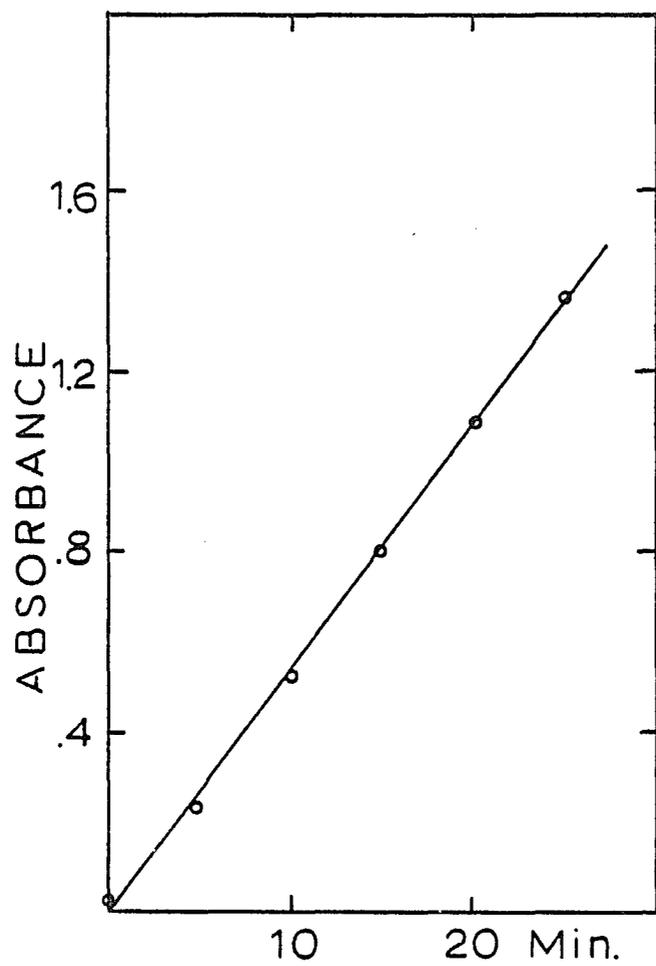


Figure 4.9. Calibration curve of SO₂ by using N₂ as carrier gas. Values on the abscissa represent the time during which SO₂ was absorbed.

The effect of temperature was also studied for nitrogen as the carrier gas. There was a 10 percent increase in absorbance from 20°C to 33°C and only a one percent increase from 33°C to 43°C.

It may be concluded, therefore, that oxygen gas interferes with this method, and in addition, there is a significant temperature dependence. It should be possible to use this method for the determination of SO_2 in air, if the SO_2 is first absorbed by molecular sieves and then desorbed (51). The desorbed SO_2 may be determined by its reaction with the copper(II)-neocuproine solution as described above. The absorption and desorption of SO_2 may be achieved by heating the molecular sieves.

It should be of interest to identify the sulfur species which is responsible for the slow reduction of Cu(II) and hence the slow formation of the Cu(I) (neocuproine)₂ complex. It should be possible to use the MECA technique to identify the various sulfur species in solution.

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