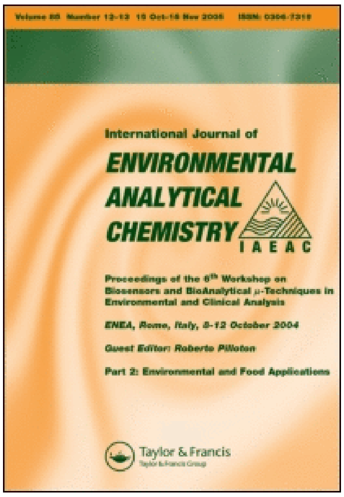

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A Spectrophotometric Method for Thioether Determination in Ambient Air

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Aqueous chloropalladate(II) solutions absorb tioether from an air flow leading to the formation of a complex extractable into benzene. The UV absorbance of the organic complex solution is proportional to the amount of thioether. Since all light thioether homologues absorb in the same spectral range with very similar molar absorptivities the method can be used for the determination of this class of compounds relevant for atmospheric sulphur cycle studies.

The preparation of test gas samples containing known amounts of di-n-propylsulphide using either capillary diffusion tubes or total evaporation of benzene-thioether solutions is described.

An interference study of some common gaseous compounds such as carbon monoxide, nitrogen oxides, carbon disulphide, carbonyl sulphide, ethylmercaptan, sulphur dioxide, dimethyl-sulphoxide, which may be present in the ambient air together with thioethers is also made.

KEY WORDS: Thioether, dialkylsulphide, sulphur cycle, spectrophotometric determination, reduced sulphur compounds.

INTRODUCTION

Biogenic emission of reduced sulphur compounds has been indicated as a point of uncertainty in any sulphur cycle model proposed.[1-8]

Recent calculations on global scale atmospheric sulphur balance, including species such as SO_2, SO_4^{2-}, COS, H_2S, $(CH_3)_2S$ and CS_2 are uncertain because available data, specially for the last three species, are sparse and show great variability.[6] Furthermore, light mercaptans, thioethers and organic disulphides, which are emitted to the atmosphere either by decomposing animal and vegetal debris in soils and natural water bodies[9-12] or by some industrial activities,[13-15] have also been omitted on that calculations. These compounds as well as some of their oxidized derivatives such as sulphoxides and sulphonic acids[16] seem to play a not negligible role in the atmospheric sulphur circulation. It is clearly necessary to gather more information about the presence of each of these species in the environment and so selective analytical methodologies are needed.

This paper describes a new method for the determination of thioethers in ambient air. A palladium(II) solution is used for collection.

The reaction:

$$R_2S + |PdCl_4|^{2-}_{aq} \rightarrow |PdCl_2(R_2S)_2| + Cl^-_{aq}$$

takes place. The complex product shows little water solubility and is easily extracted into benzene, and its concentration in the organic phase can be determined spectrophotometrically.

Table I indicates some spectral properties of light alkyl thiothers. The similarities enable convenient application of the proposed spectrophotometric method to the "class" of low molecular weight alkyl thioethers rather than to a particular member. The final result can also be expressed in mol number or mass of sulphur present in the sample because of this particular kind of chemical properties.

EXPERIMENTAL

The basic apparatus used for laboratory experiments with test gas mixtures is shown in Figure 1. Air is pumped through cleaning

TABLE I

Physical data for some light thioethers (R_2S). Boiling points and molar absorptivities (ε) of species $|PdCl_2(R_2S)_2|$ in benzene solutions at wavelength of maximum absorption (λ_{max})

R_2S	B.P.[a] °C	ε $L\,cm^{-1}\,mol^{-1}$	λ_{max} nm
dimethylsulphide	37.3	14.5×10^3[a]	303[b]
di-n-propylsulphide	142.8	14.7×10^3[c]	308[c]
di-i-propylsulphide	119	14.5×10^3[b]	310[b]

[a] From reference 17.
[b] From reference 18.
[c] Own data.

cartridges and reaches the diffusion chamber where a capillary dispenser tube containing a thioether may be installed. Alternatively in this chamber total evaporation of 1 cm^3 aliquots of benzene-thioether solutions can be achieved. Thermostating is afforded within 0.1°C for the diffusion chamber. Downstream the thioether source two bubblers are mounted each containing 5 cm^3 of the absorbing solution which is 2.3×10^{-3} M in $PdCl_2$ and 0.1 M in HCl. The air flow is held at 180 $cm^3\,min^{-1}$ by a proper critical orifice. Glass was the main material employed. When using the thermostat a metallic coil affords pre-equilibration of the airflow before it reaches the diffusion chamber. Plastic (tygon R type) tubing connexions are held as short as possible.

Construction details of the chamber and the capillary dispenser as well as of the bubblers are given in Figure 2.

The extraction procedure is carried out with portions of 1 cm^3 benzene which are shaken for 5 minutes with the aqueous phase in the bubbler and then transferred with the aid of a Carlton type pipette.[19] The volume is made up to 10 cm^3 for the photometric readings. Good quality volumetric glassware was used with no further care. For the photometric measurements quartz cuvettes of 10 mm optical path length were used in a Beckmann DBG recording spectrophotometer and in a Zeiss PMQ-2 spectrophotometer.

All reagents used were of analytical grade, except di-n-propylsulphide which was properly distilled before use.

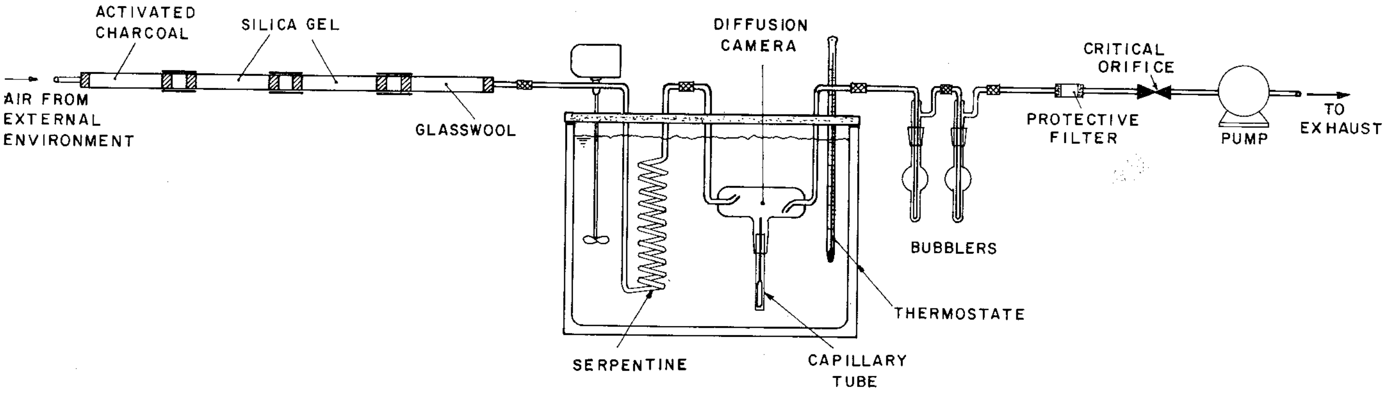
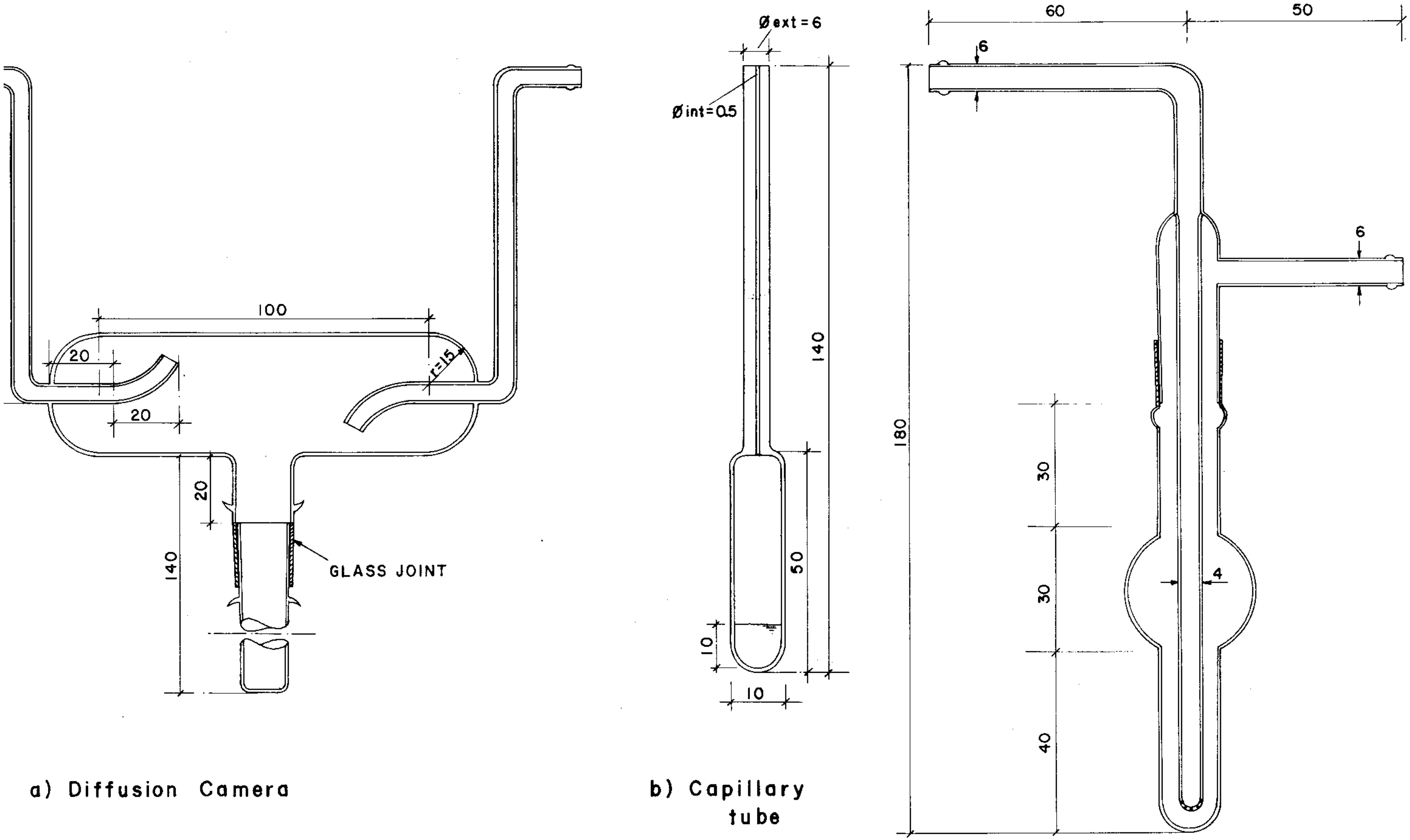


FIGURE 1 Basic apparatus for laboratory experiments.



a) Diffusion Camera

b) Capillary tube

c) Bubbler

FIGURE 2

RESULTS AND DISCUSSION

Preparation of "reference" $|PdCl_2(R_2S)_2|$ extracts

One cm^3 benzene solutions carefully prepared with known amounts (between 10–100 μg) of di-n-propylsulphide (DnPS) were thoroughly shaken with equal volumes of aqueous solutions 2.3×10^{-3} M in $PdCl_2$ and 1 M in NaCl at pH = 1, adjusted with HCl. Organic layers containing the $|PdCl_2(R_2S)_2|$ complex (where R = n-propyl) are produced. Experiments carried out have shown that at least 60 minutes are necessary for completion of this reaction and that better results are obtained with four subsequent washings of the aqueous phases with 1 cm^3 benzene portions. The final volume is then adjusted to 10 cm^3 with benzene for the photometric reading. From these experiments and previous knowledge of the behavior of this kind of compound,[18] the absorbance values at 308 nm of the organic phases such obtained were considered to correspond to 100% recovery of the DnPS. Accordingly the data shown in Table III allow to calculate the molar absorptivity of $|PdCl_2(R_2S)_2|$ (R = n-propyl) which is found to be 14.7×10^3.

TABLE II
Collection of DnPS in $|PdCl_4|^{2-}$ absorber solutions

	Absorbance of benzene extracts	
Sample number	1st bubbler	2nd bubbler
1	0.607	0.026
2	0.513	0.044
3	0.434	0.045
4	0.395	0.025
5	0.391	0.060
Average	0.468	0.040
Standard deviation	0.094	0.015

Amounts of DnPS sampled: 48 μg.

This type of extraction procedure was systematically used to obtain "reference" values for calibration.

TABLE III

Sampling of DnPS from test gas atmospheres

m	C	A_R	A_1	A_2	$(A_1/A_R) \times 100$	$(A_1 + A_2/A_R) \times 100$
12.5	10	0.142	0.134	0.009	94	101
25	20	0.281	0.271	0.006	96	99
37.5	30	0.438	0.412	0.006	94	95
50	40	0.638	0.574	0.016	90	92
62.5	50	0.744	0.718	0.006	96	97

m: total mass (μg) of sampled DnPS for 24 hours.
C: average concentration (ppbv) of thioether in the air flow.
A_R: absorbance values of the corresponding "reference" (see text) samples.
A_1, A_2: absorbance values read on the extracts of the 1st and 2nd bubblers.

Collection studies employing a capillary dispenser for test gas preparation

In an apparatus like that depicted in Figure 1 laboratory air is pumped at controlled flow through activated charcoal, silica gel and glass wool filters. Inside the diffusion chamber, which is immersed into a constant temperature water bath, the air passes over the capillary dispenser (containing DnPS in its bulb) and picks up DnPS vapor. After a period of time the mass loss of the capillary tube gives the amount of thioether vapor diffused into the air stream. Di-n-propylsulphide is used instead of dimethylsulphide—which would be preferable from the environmental point of view—because big errors are inherent in the application of diffusion arrangements containing compounds of very low boiling point.[20] The use of DnPS however has no inconveniences regarding the spectral similarities shown in Table I.

Before starting the sampling the entire apparatus has to be "preconditioned" for a period of time with an atmosphere containing sulphide vapors. Laboratory observations indicate that the concentration of these vapors in the preconditioning phase is irrelevant, but if the humidity of the air stream is over 70% the measurements show a large standard deviation and the diffusion rate through the capillary seems to become lower. The influence of humidity on the adsorption of sulphide compounds on glass surfaces has been reported.[21]

The diffusion rate of DnPS through the capillary tube was determined to be $0.16 \pm 0.03\,\mu g\,min^{-1}$ (at 20°C). At a flux of $180\,cm^3\,min^{-1}$ the concentration of DnPS in the air stream is $890\,\mu g\,m^{-3}$ and in a sampling time of 5 hours a total amount of $48\,\mu g$ of the thioether goes to the bubblers. Since molar absorptivity is 14.7×10^3 the absorbance would be 0.598 in a $10\,cm^3$ benzene solution. Table II shows the experimental data obtained under these conditions. The average measured values and corresponding standard deviations are 0.468 and 0.094 in the first impinger and 0.040 and 0.015 in the second one giving $78 \pm 16\%$ efficiency for the first absorbing bubbler only and $85 \pm 18\%$ for both. Though these figures include also uncertainties due to the performance of the capillary dispenser calibration they may be considered as a measure of the collection efficiency of the palladium solution used.

Collection studies employing total evaporation of di-n-propylsulphide solutions

A sample of $1\,cm^3$ DnPS-benzene solution of known concentration is put inside the diffusion chamber, and a stream of clean air is passed over it until complete evaporation has taken place. Thermostating is not necessary. The solution can be placed either in the main body of the chamber or in its neck (see Figure 2a) thus requiring short or long periods of time to evaporate completely. Benzene vapor prevents adsorption of the thioether on the glass walls of the apparatus (Benzene in fact displaces any thioether previously adsorbed!). So in this case pre-conditioning as well as drying the air stream is not necessary. At the same time dispersion of the results is minimized (see Table IV). These advantages lead to the election of this mode of operation as the procedure to achieve the calibration plot curve.

Higher collection efficiences are attained with palladium and chloride concentrations of $2.3 \times 10^3\,M$ and 0.1 M, respectively. Optimum pH for the reaction is between 1 and 4.[18] So the absorbing solution was chosen to be $2.3 \times 10^{-3}\,M$ in $PdCl_2$ and 0.1 M in HCl.

Table III summarizes data for a calibration plot. Various amounts of DnPS in benzene were evaporated in an air flow of $180\,cm^3\,min^{-1}$ in 24 hours. Absorbances obtained after extraction into benzene of

TABLE IV

Repetitive measurements employing evaporation of DnPS-benzene solutions for test gas production

	Absorbance readings of the extractions	
Sample number	1st bubbler	2nd bubbler
1	0.585	0.005
2	0.575	0.023
3	0.575	0.010
4	0.570	0.066

Amounts of DnPS sampled: 50 μg.

the content of each of two bubblers in series are tabulated as well as the absorbances of the corresponding "reference" samples obtained as described previously. The average concentrations of the thioether in the air stream are also shown.

Recoveries are higher in this case than that obtained when the thioether source was the capillary dispenser and benzene was absent. Statistical tests indicate that the additional absorbance resulting from the second bubbler does not contribute significantly to the values given by the first impinger only. Table IV shows the repetitivity of results.

Solution components stability

Experiments have shown that after thioether collection in an aqueous palladium solution the same results are obtained regardless whether the benzene extraction is carried out immediately or if it is delayed for 15 days, provided the solution is kept in the dark. The organic extract, once obtained, keeps constant absorbance by at least 30 days, if kept in the dark.

Interference study

Each of the following substances introduced into a flow of air containing known quantities of DnPS does not cause significant changes of the results:[22] hydrogen sulphide, carbon monoxide, carbonyl sulphide, nitrogen oxides, carbon disulphide, ammonia, ethylmercaptan, sulphur dioxide.

H_2S, CO and COS were tested in great excess over DnPS so that in each case a precipitate was formed in the palladium solution. The benzene extraction, however, could be carried out in the normal way. Nitrogen oxides (from reaction of metallic copper with nitric acid) were introduced into the chamber containing thioether vapor in such high amounts that the typical brown colour could easily be seen. But no interference was observed. CS_2, NH_3 and ethylmercaptan were applied in 100 fold excess with respect to DnPS but no adverse effects could be identified. Ethylmercaptan produces a yellow precipitate in contact with palladium solutions. This compound must be allowed to "age" by 48 hours before carrying out the benzene extraction in order not to influence the spectrophotometric measurements. SO_2 in concentrations 1000 times higher than those of the thioether does not interfere with the determination.

Dimethylsulphoxide (DMSO) in concentrations 40 times higher than the DnPS concentrations generates results which are higher by 7%. DMSO, however, scarcely exceeds the thioether concentrations in the atmospheric environment[23] and therefore is not expected to interfere considerably.

PROCEDURE FOR FIELD SAMPLING

The set up for field sampling requires a pump to drive an ambient air flow through a bubbler (containing 2.3×10^{-3} M $PdCl_2$ and 0.1 M HCl aqueous solution) and a device to control the flow rate (e.g. a critical orifice).

With an air flow of $180 \, cm^3 \, min^{-1}$ and $5 \, cm^3$ of absorbing solution one can collect 24 hour samples. To avoid thioether adsorption losses on tubing it is recommended to pull the ambient air directly through the bubbler. Light protection is not necessary. These conditions are designed for thioether levels between 3 and 50 ppbv in air. After collection the solution can be stored for at least 15 days in the dark before extraction takes place.

Usually the extraction is carried out after two days. Five $1 \, cm^3$ benzene portions are successively shaken for 5 minutes with the aqueous solution in the bubbler and transfered to a 10 cm^3 volumetric flask which is then filled up to the mark with benzene. The spectrophotometric measurement is carried out in cells of 1 cm optical path length against a benzene blank if the solvent used is of spectorscopical quality. Using pro-analysis grade solvent a parallel reagent blank must be run. As the dimethylsulphide is the thioether of highest abundance in ambient air, the absorbance must be read at 303 nm which corresponds to the maximum molar absorptivity (14.5×10^3) of the respective palladium complex.

Following the procedure given in this paper the concentration of thioether in air at standard pressure and temperature is given by:

$$\text{Thioether concentration (ppbv)} = 65.0 \times \text{Absorbance reading.}$$

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