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SOLIDS COATED WITH SODIUM TETRACHLOROPALLADATE: SORBENTS FOR REDUCED SULFUR COMPOUNDS IN AIR

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A study of the preconcentration of tioethers in air by means of the passage of gas flow on solid sorbents coated with sodium tetrachloropalladate was undertaken with the aim of achieving chemical fixation. This fixation presented high specificity and blocked the migration of the sorbed compound through the other active sites. The species obtained were selectively dissolved in organic solvents, resulting in the sulfur reduced compound concentration in the organic phase, which could be determined spectrophotometrically.

KEY WORDS: Solid sorbent, sulfur reduced compound determination, sulfur cycle, sulfur compounds, pre-concentration, spectrophotometric determination, organic sulfides.

INTRODUCTION

Since the first Sulfur Cycle Model¹, the biogenic reduced sulfur compounds were considered the main route for the entrance of sulfur into the atmosphere. Up to now, among those compounds, the dialkylsulfides and mainly the dimethylsulfide, were considered the "lost link" necessary to balance the sulfur cycle^{2,3}. The knowledge of the chemistry of sulfur compounds in the environment has taken a greater significance because they are involved in the formation of atmospheric aerosols, acid precipitation and recently^{4,6} it has been suggested that the presence of sulfur compounds in the atmosphere play an important role in the global temperature control due to possible changes in the solar radiation balance. Therefore, the importance of a clear understanding of biogenic sulfur emission rates in the sulfur cycle is obvious. Studies published in the last decade have shown great discrepancy in the amount of sulfur necessary to balance the cycle^{7,9} indicating that the problem is not resolved.

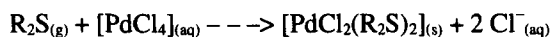
Analyses of air samples for gaseous sulfur constituents at low concentrations are complicated, among other problems, by the large number of chemical compounds present at trace level. Different techniques have been used in the analyses of reduced organic sulfur gases, but they usually involve the use of cryotrapping and a flame photometric detector (FPD) operating in the sulfur specific mode¹⁰.

Detection is only a step in the analytical method. However, for many years, selectivity and specificity were the main requirements for those issues. The increased environmental concern called for new analytical alternatives, and selective sampling (previous specification) and preconcentration became probably the more important steps in the environment analytical process. Therefore selectivity or specificity requirements were also displaced to these stages¹¹. Procedures described in this paper were developed in accordance with these analytical criteria.

EXPERIMENTAL

Principles of method

A new selective sampling method was developed based on the transformation¹²:



The resulting complex is slightly soluble in water, though soluble in organic solvents. The solutions presented well defined absorption maximum in the near U.V. region (around 300 nm) and absorbance values were proportional to the amount of sulfur reduced compounds¹². The spectral similarity of the organic solutions of the complexes formed with low molecular weight alkyl thioethers has shown the possibility to express the spectrophotometric response in terms of mols or sulfur mass collected¹³.

To avoid field sampling problems such as palladium solution drying-out during long term samplings¹³ a new device was developed and tested. Glass wool coated with sodium tetrachloropalladate was proved to be a very efficient tool for the selective collection of sulfur reduced species.

Sample collection

Following the standard gas mixture production based on the diffusion method^{13,14}, diffusion rate for the di-*n*-propylsulfide (British Drug House Ltd. properly distilled before use) was $4.10 \pm 0.3 \text{ nmols} \cdot \text{min}^{-1}$, when determined at $35.5 \pm 0.1^\circ\text{C}$ and the carrier gas flow held at $158 \text{ cm}^3 \cdot \text{min}^{-1}$.

The similarities of spectral properties of $[\text{Pd}(\text{R}_2\text{S})_2\text{Cl}_2]$ formed for light alkyl thioethers enable the use of the di-*n*-propylsulfide¹²⁻¹³.

Analytical procedure

For selective sampling the basic idea was packing a sorbent tube with different large surface solid substrates coated with sodium tetrachloropalladate in order to select the best support. The sorbent tube was made of Teflon (0,4 cm - internal diameter and 4,0 cm length) and a brass ferrule was fitted on each end. The packing substrates were held inside the tube by glass wool previously silanized¹⁵ with methyldichlorosilane (Merck).

The coating solutions were initially prepared with 0.6 mmol of PdCl₂, 1.2 mmol NaCl and 55 ml of 0.10 mol.l⁻¹ hydrochloric acid. Two types of silica-gel (0.2 – 0.5 mm and 1 – 3 mm) were used as substrates. The sorbent was prepared by adding 1 silica-gel to the solution. The resulting mixture was dried at 60°C in a stove with air circulation. At the end of the drying process the solution should be stirred to guarantee the more homogeneous Na₂[PdCl₄] deposition on the surface of the sorbent.

The sorbent tube was connected to the streamline of the di-n-propylsulfide gas mixture standard. After collection, the packing substrate was transferred to an extraction tube. The sorbent tube was shaken with about 1 ml toluene. This solution was transferred to a 5.0 ml volumetric flask with the aid of a Carlton type pipette¹⁶. This was carried out at least five times to ensure complete dissolution and total removal of the [(R₂S)₂PdCl₂] species. After having adjusted the volume to 5.0 ml, the photometric measurement was taken at 306 nm using quartz cuvettes of 10.0 mm optical path length with a Varian-Cary 219 spectrophotometer. The blank was obtained by reproducing the previous steps with a proper substrate/Na[PdCl₄] amount. Data obtained from the use of these two types of substrate did not show repeatability and proportionality.

In the course of these experiments some unusual facts lead to try the use of the glass wool as possible substrate, since the yellow species [(R₂S)₂PdCl₂] was apparently formed in the contact border substrate/glass wool. Consequently, a new substrate (the glass wool—fiber medium) was tested. In the preparation of this new sorbent, similar procedures and equal amount of reagents were used. Results of the use of this solid sorbent then showed repeatability and proportionality and subsequent experiments were made using the new solid sorbent.

RESULTS AND DISCUSSION

Amounts of reagents of coating solution

Coating solutions were prepared with different NaCl amounts. In this manner the procedure was repeated, but using for each 0.6 mmol of PdCl₂ 1.2, 1.4, 2.6, 5.1 and 7.7 mmol of NaCl. Under these conditions the presence of Na₂[PdCl₄] species was warranted and the solution was used to coat 1.0 gram of glass wool (fiber medium). Among the above sorbents, the 0.6 mmol PdCl₂:5.1 mmol NaCl preparation proved to be the best choice (Table 1).

Table 1 Amounts of PdCl₂ and NaCl used for preparation of sorbent wool. Time of sampling 20 minutes.

<i>Rates of PdCl₂:NaCl mmol</i>	<i>Absorbance 306 nm</i>
0.6 : 1.2	0,118
0.6 : 1.4	0,112
0.6 : 2.6	0,136
0.6 : 5.1	0,158
0.6 : 7.7	0,160

Amounts of reagent-coated sorbent

Collection capacity of different sorbent weights and different PdCl₂/NaCl amounts, but maintaining the same molar proportion was evaluated. These experiments were carried out in a sorbent tube with two sorbent layers separated by glass wool. The backup sorbent layer functioned to signal the breakthrough of the front layer. The front and backup sections of the tubes were analysed separately.

The results (Table 2) showed that the sorbent maintains the complete retention capacity for the R₂S, and also proved that the amount of coating material initially used (about 3×10⁻² g) was far from breakthrough. In real sampling, dust and other compounds are expected to interact with the sorbent, reducing the collection capacity.

Table 2 Sampling for 30 minutes, using different amounts of PdCl₂ and sorbent. Absorbance of backup layer was always insignificant.**Table 2a** Sorbent tube with different amounts of sorbent weight.

<i>Amounts PdCl₂/sorbent weight mmol</i>	<i>Absorbance 306 nm</i>
1,2	0,169
0,6	0,178
0,4	0,178

Table 2b Surface sorbent with different amounts of PdCl₂ for gram of solid sorbent.

<i>Amount of coating material(*) g</i>	<i>Amount of reagent coated sorbent umol</i>	<i>Absorbance 306 nm</i>
6,3	25,2	0,175
3,2	12,8	0,170
1,5	6,0	0,165
1,1	4,4	0,180

(*) prepared with 0,4 mmol of PdCl₂ for gram solid sorbent.

Table 3 Effect of carrier gas flow in sorbent retention. Time of sampling 20 minutes.

Carrier gas flow ml. min^{-1}	Absorbance (front) 306 nm	Absorbance (backup) 306 nm
158	0,158	-
571	0,180	-
3200	0,375	-

Effect of the carrier gas flow rate

The effect of the carrier gas flow on the retention capacity was also evaluated by analysis of the front and backup section. This effect was studied in this manner because of the difficulty in handling properly the standard gas, as diffusion rate is dependent on the carrier gas flow¹⁴. This difficulty was overcome by using a backup sorbent. Positive signs in this section would mean that the sorbent did not maintain its retention capacity. Results in Table 3 show an increase in the amount of R_2S found in the front section brought about by the increase in carrier gas flow and indicate that the retention capacity was kept even for larger flows.

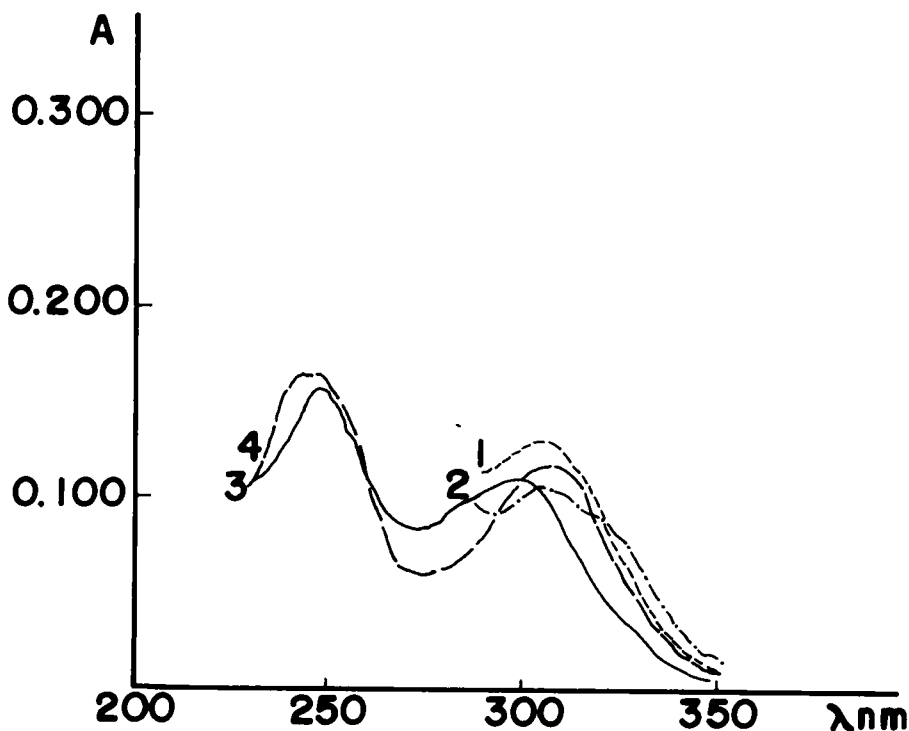


Figure 1 Absorption spectra of $[\text{Pd}(\text{R}_2\text{S})_2\text{Cl}_2]$ in (1) toluene (2) benzene, (3) *iso*-octane and (4) dichloromethane, Time of sampling 20 minutes. Flow of standard gas mixture 158 ml. min^{-1} .

Considerations on solvent used

According to the methodology proposed initially¹³, benzene was used as solvent for the extraction of $\text{Pd}(\text{R}_2\text{S})_2\text{Cl}_2$ in aqueous solution. Later, this hazardous solvent was substituted for toluene. Other solvents were also tested: dichloromethane and *iso*-octane. These were transparent at wavelengths shorter than 185 nm and presented also distinct polarities. The absorption spectra of $[\text{Pd}(\text{R}_2\text{S})_2\text{Cl}_2]$ in these solvents are shown in Figure 1.

Interference study

For a $10^{-10}\%$ concentration level, about 10^5 different compounds can be found in a sample of atmospheric air¹⁷. The use of a chemical compound like the Na_2PdCl_4 as sorbent would reduce most of the interferent compounds to those showing to have chemistry affinity with this salt. Certainly, based on this assumption, Fagá¹³ selected a set of compounds of recognized importance and global distribution which showed chemical affinity with aqueous solution of Na_2PdCl_4 . However, as in the present study the interaction was in the gas/solid interphase, evaluations of interferent compounds were repeated for further confirmation.

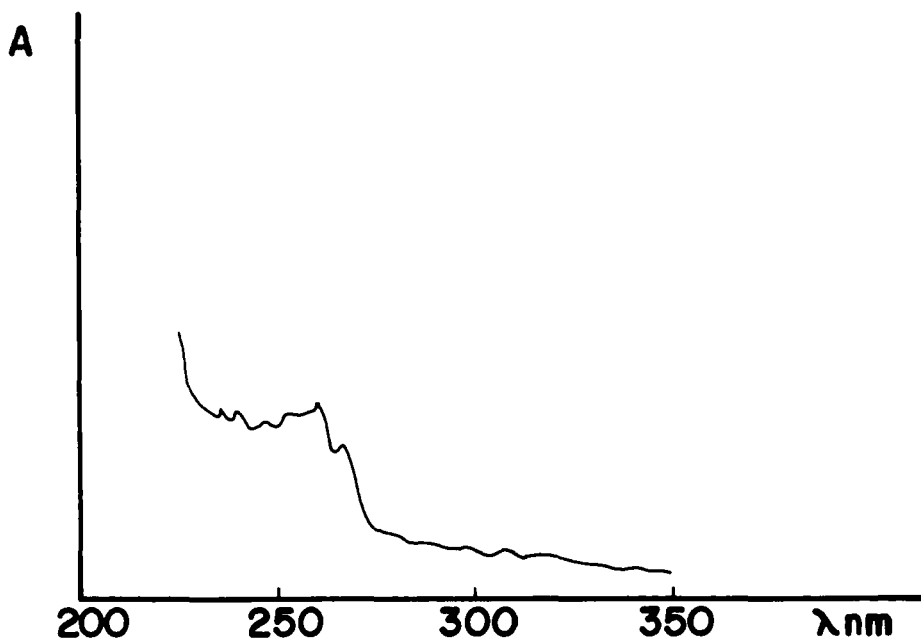


Figure 2 Absorption spectrum of the compound formed by interaction of nitrogen oxides and sorbent, in dichloromethane.

Inorganic compounds

Gases such as hydrogen sulfide, carbon monoxide, carbonyl sulfide, carbon disulfide, ammonia, sulfur dioxide did not cause interference because either they did not react with the reagent coated or did not produce compounds soluble in the solvents used to extract the $[\text{Pd}(\text{R}_2\text{S})_2\text{Cl}_2]$ species. Nitrogen oxides (from reaction of metallic copper with nitric acid) reacted with the coated reagent, but the resulting compound was only dissolved by dichloromethane (Figure 2). However, the nitrogen oxides are oxidant and could also be able to react with the R_2S fixed in the sorbent evaluated.

In this manner as a first step, samples of the standard R_2S gas were taken. Then, air with nitrogen oxides was passed through the sorbent tube. The absorption spectrum of this product is shown in Figure 3. This Figure shows that nitrogen oxides did not react immediately, despite the high concentration of nitrogen oxides (quite different from environmental systems) shown by the brown color formed when the air flow was shut off. Possibly, it occurred because the nitrogen oxides preferably react with a Na_2PdCl_4 species. When the reaction occurred in aqueous solution, these nitrogen oxides did not react with a $\text{Pd}(\text{R}_2\text{S})_2\text{Cl}_2$ species¹⁸, being another probable evidence of their preference for the Na_2PdCl_4 .

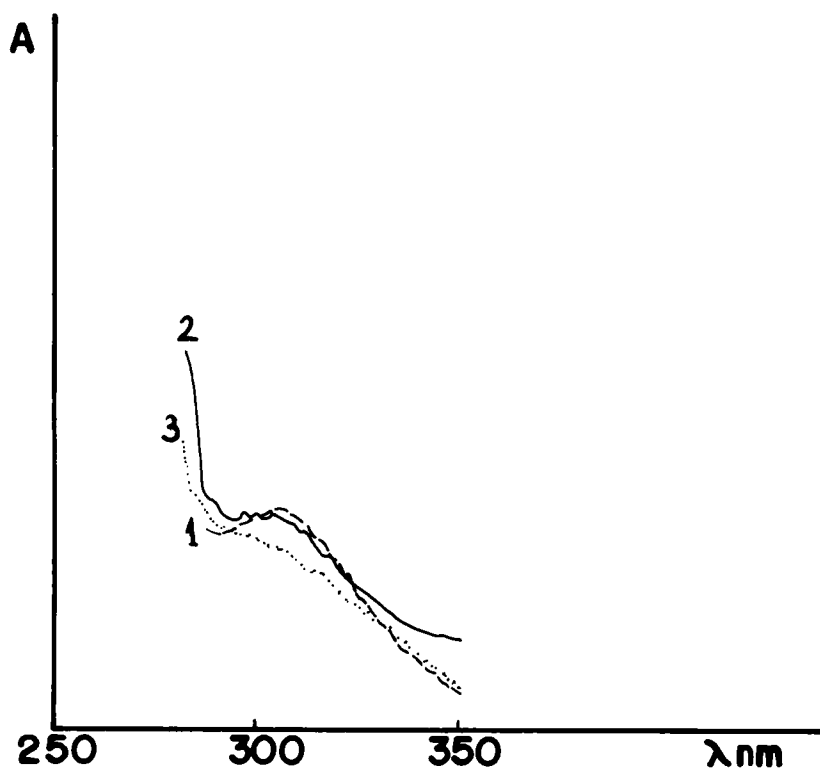


Figure 3 Absorption spectra, in toluene, of compounds formed from the reaction of nitrogen oxides and R_2S retained on sorbent. The time that the mixture nitrogen oxides and air flow through the sorbent tube were in contact, were (1) 5 minutes, (2) 10 minutes and (3) 20 minutes.

Organic Compounds

Dimethylsulfoxide reacts with the sorbent and the absorbance spectrum of the product is shown in Figure 4. The species formed is only practically soluble in dichloromethane. Ethylmercaptane reacts also with the sorbent, but the solubility is also effective in dichloromethane (Figure 5). Faga¹⁷ showed that in aqueous solution the proportion between the amount of reagents in this kind of compound is important. For ratios smaller than 1.6 μmol ethylmercaptane per 11.5 μmol Na_2PdCl_4 , compounds with absorbance at 306 nm are not formed.

Methodology validation for dimethylsulfide analysis in air

Taking into account that the dimethylsulfide is the more common organic sulfide found in the air, the collection device proposed was used to collect air samples containing the mentioned sulfide.

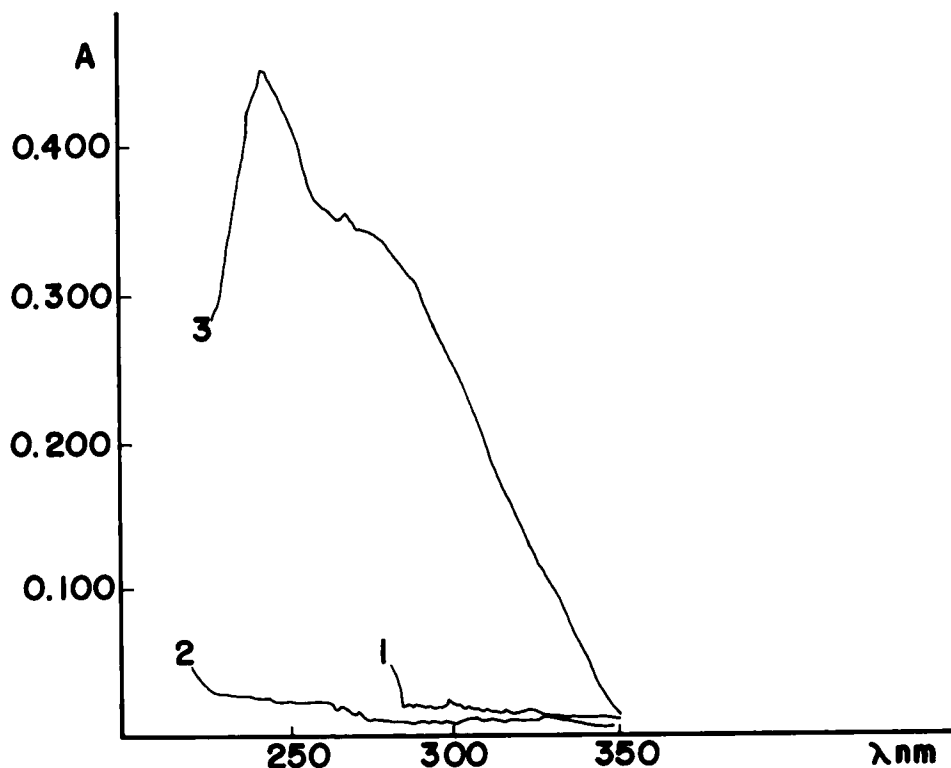


Figure 4 Absorption spectra of compounds formed by interaction of dimethylsulfoxide and sorbent in: (1) toluene, (2) *iso*-octane, (3) dichloromethane.

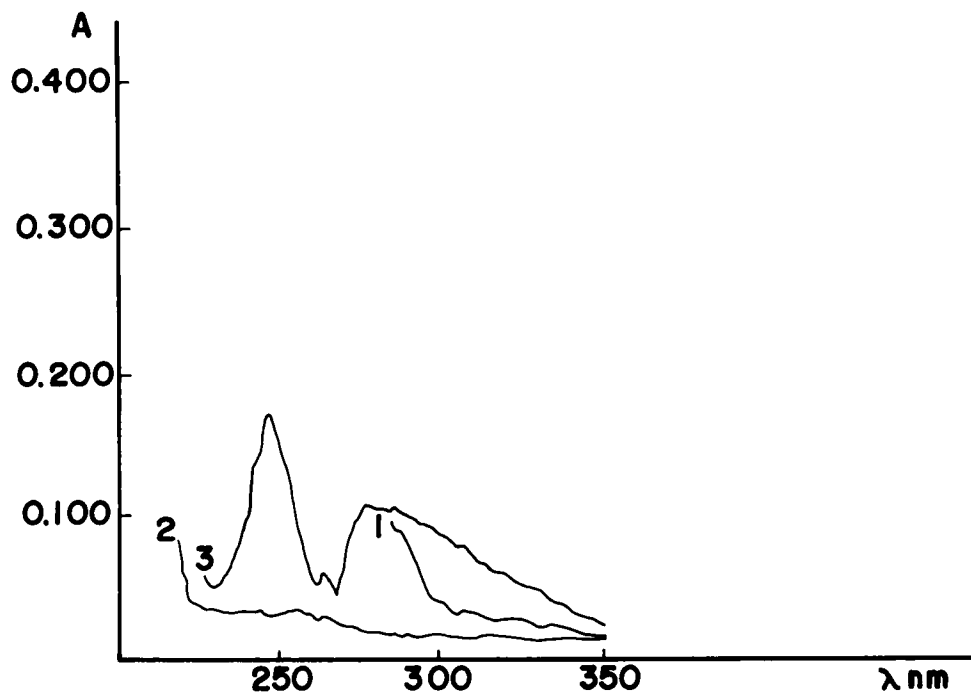


Figure 5 Absorption spectra of compounds formed by interaction of ethylmercaptan and sorbent in: (1) toluene, (2) *iso*-octane, (3) dichloromethane.

The permeation tube proposed by Teckentrup and Klockow¹⁹ containing dimethylsulfide (Aldrich) was used as a source of constant quantity of this sulfide. This was used, besides the difficulty to know the permeation rate, due to the long sampling period required¹⁹.

Air/dimethylsulfide samples showed the expected behaviour during three different sampling periods 15, 30 and 60 minutes. In each period the sulfide amounts collected were constant and furthermore they kept proportionality (Absorbance 0,136; 0,276 and 0,547, respectively). The species $[\text{PdCl}_2 \cdot 2(\text{H}_3\text{C})_2\text{S}]$ extracted with toluene showed well defined absorption maximum at 303 nm¹².

CONCLUSION

The Na_2PdCl_4 coated on glass wool can be used for pre-concentration of reduced sulfur compounds in the air. For determination of thioethers as dimethylsulfide, the $[\text{Pd}(\text{R}_2\text{S})_2\text{Cl}_2]$ must be dissolved in toluene. This solvent does not dissolve the other possible compounds formed from the interaction of sorbent/interferent. In this case, for optimum sensitivity, a wavelength of 306 nm has to be employed. Figure 6 shows the calibration plot from 0 to 615 nmols of di-*n*-propylsulfide. The concentration and flow rate were constant but sampling

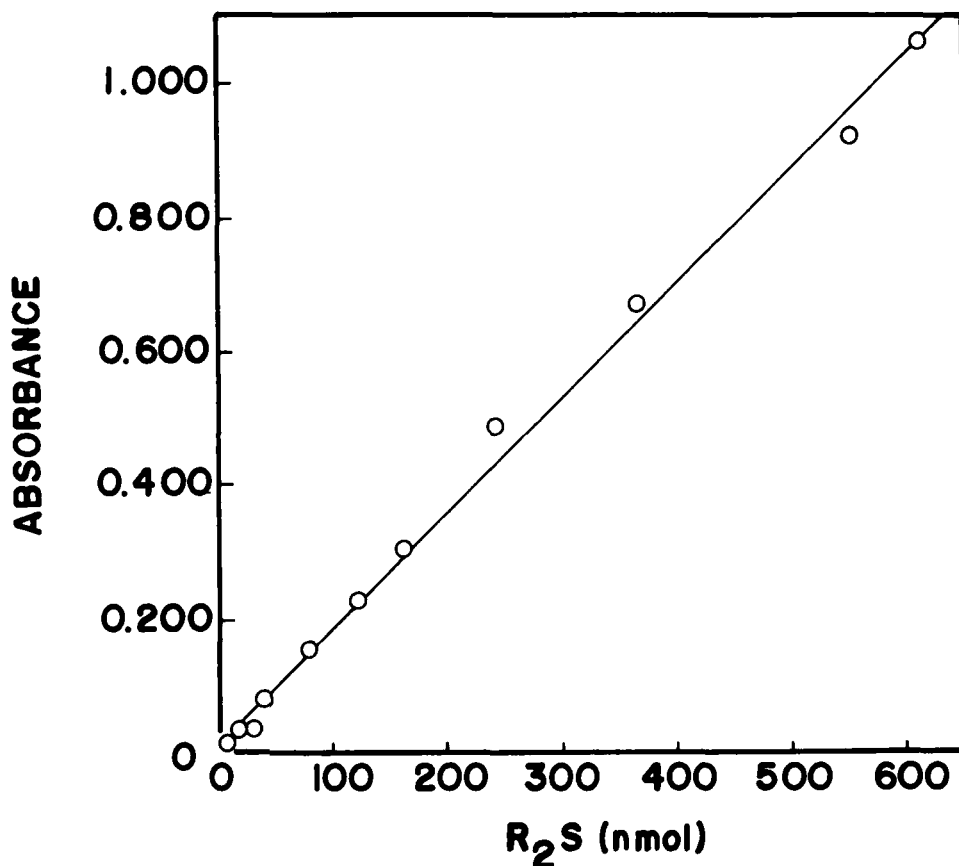


Figure 6 Calibration plot for R₂S concentrations in air obtained with constant flow rate but varying the sampling duration. Solvent: toluene.

duration was varied. The equation of the calibration graph obtained by the method of least squares was $A = 0,015 + 17,1 \times 10^{-4} \text{ nmol R}_2\text{S}$.

This method for determination of thioethers is fast and specific, requires minimal sample treatment and instrumentation. Therefore, it offers a good alternative for determination of thioethers in the environment. In samples containing high concentrations of oxidant gases, scrubbers have to be used to remove the oxidants from the air.

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