

## SPECTROPHOTOMETRIC DETERMINATION OF DIMETHYL DISULFIDE IN AIR POLLUTANTS FROM THE RUBBER INDUSTRY

Anna TUREK<sup>1</sup>, Monika SKRZYDLINSKA<sup>2</sup> and Bogdan PTASZYNSKI<sup>3</sup>

*Institute of General and Ecological Chemistry, Technical University, 36 Zwirki Str. 90-924, Lodz, Poland*

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A spectrophotometric method was developed for the determination of dimethyl disulfide (DMDS) in complex gas mixtures emitted by the rubber industry. The method allows organic disulfides to be quantitated in amounts exceeding 1.5 mg/m<sup>3</sup> gas (expressed as DMDS) and can be applied to the determination of disulfides in air at workplace as well as in gaseous products of thermal and biological decomposition of solid substances. The method enables disulfides and mercaptans to be determined simultaneously.

**Key words:** Dimethyl disulfide; Spectrophotometric determination in air; Rubber industry.

Technological processes of the rubber industry are associated with the emission of volatile substances which have a negative effect on the human organism and cause environmental pollution. This primarily concerns the process of vulcanization, where various odorous and toxic compounds are produced by thermal decomposition of antiaging substances, vulcanizing agents and flexibilizers. Since the composition of the emitted gases is complex and the concentrations are low, they can only be quantitated by highly selective and sensitive methods. Conventional methods described in the literature are largely applicable to single compounds but not to their mixtures. Their application to the determination of complex gas mixtures often requires substantial modifications.

One of the toxic compounds present among air pollutants from the rubber industry is dimethyl disulfide (DMDS), a flammable compound with an unpleasant odour which is harmful to the skin, eyes and the respiratory tract. In the emitted gases, DMDS is present together with other sulfur compounds of similar properties such as mercaptans, sulfur dioxide and hydrogen sulfide, which aggravate seriously its determination. The purpose of the present work was to modify the method for the determination of mercaptans<sup>1</sup> so as to make it applicable to the quantitation of DMDS in air at workplace in rubber plants. The determination of mercaptans is based on the reaction of the thiol with nitrous acid giving the corresponding thioazo acid ester (the excess HNO<sub>2</sub> is decomposed under the influence of amidosulfuric acid). The ester is decomposed in the

presence of Hg(II) salts to give  $\text{HNO}_2$  in an amount equivalent to that of the mercaptans. This acid is reacted with sulfanilic acid and *N*-(1-naphthyl)ethylenediamine dihydrochloride to form a coloured azo compound, whose absorbance is measured at 605 nm.

## EXPERIMENTAL

### Reagents and Apparatus

DMDS solutions in methanol were prepared in concentrations of 7.7  $\mu\text{g/ml}$  and 77  $\mu\text{g/ml}$ . If stored at 5 °C, the solutions remained stable for a minimum of 1 month.

Solution A: 1 : 9 (v/v) mixture of 0.01 M  $\text{NaNO}_2$  and 1 M  $\text{H}_2\text{SO}_4$ .

Solution B: 0.5 wt.% amidosulfuric acid.

Solution C: 1 : 4 (v/v) mixture of 1 wt.%  $\text{HgCl}_2$  and 0.5 wt.% sulfanilic acid in 0.4 M HCl.

Solution D: 0.1 wt.% *N*-(1-naphthyl)ethylenediamine dihydrochloride in 0.4 M HCl.

Dithizone, 0.1 wt.% solution in 96 vol.% ethanol.

*o*-Hydroxymercuriobenzoic acid<sup>2</sup> (HMB), 0.05 M solution. 16 mg of *o*-hydroxymercuriobenzoic anhydride was dissolved in 100 ml of 1 M NaOH and diluted to 1 l with water. The concentration of the substance was determined as follows: 20–80 mg of *N,N'*-diphenylthiourea were dissolved in 20 ml of ethanol, 2 ml of 1 M NaOH were added and the whole was heated in boiling water for 1 min. The system was titrated with the solution of HMB in the presence of dithiozone until the colour changed from yellow to red (pH 12–13). The  $1 \cdot 10^{-4}$  M HMB solution was obtained by diluting 0.05M HMB.

Zinc amalgam: 6 M HCl was poured on 100 g of zinc (20 mesh) and allowed to stand for 1 min. 30 mg of  $\text{HgCl}_2$  were added, stirred and in 1 min the amalgam was washed with water until no acid reaction was observed any more. Stored in dry conditions, the amalgam was stable for a minimum of one month.

Reduction column<sup>3</sup>: a glass tube 75 mm long, 15 mm i.d., closed on both ends with ground-in stoppers, filled with zinc amalgam up to  $h_1 \approx 40$  mm. Prior to use, the efficiency of the amalgam was tested as follows. A standard sample containing 50–100 mg of DMDS was placed in the column, 2 ml of 1 M  $\text{H}_2\text{SO}_4$  were added and the column was closed with stoppers. In 5 min during which the reduction took place, the solution was transferred into a flask containing 10 ml of 1 M NaOH and 2 ml of a saturated aqueous solution of EDTA. The column was washed with  $2 \times 5$  ml of 0.25 M  $\text{H}_2\text{SO}_4$  and the eluate was added to the same flask. The combined solutions were titrated with  $1 \cdot 10^{-4}$  M HMB in the presence of dithizone until the colour changed from yellow to red (pH 12–13). If the reduction was found incomplete, the amalgam was replaced with a fresh preparation. In routine determinations, the amalgam was tested in this manner every two or three days. After each reduction the column was washed consecutively with 2 M  $\text{H}_2\text{SO}_4$  and water until no acid reaction was observed.

Spekol 11 spectrophotometer (Zeiss, Jena). The measurements were performed using cells 1 cm optical pathlength.

### Calibration Line

DMDS in a quantity over 15  $\mu\text{g}$  dissolved in 5 ml of methanol was pipetted into the reduction column, 2 ml of 1 M  $\text{H}_2\text{SO}_4$  were added, and the column was closed. The reduction was allowed to proceed for 5 min. The whole volume of the solution after reduction was transferred into a 50 ml volumetric flask containing 5 ml of solution A. The column was washed with  $2 \times 5$  ml of 0.25 M  $\text{H}_2\text{SO}_4$  and the eluate was poured into the same flask. One ml of solution B was added, the mixture

was stirred for 30 s, 10 ml of solution C were added, and the whole was diluted to volume with solution D. The absorbance of the solution was measured in 30 min at a wavelength of 605 nm against a reagent blank. The results of determination are given in Table I.

The absorbances of the standard solution at a concentration of 5.40  $\mu\text{g DMDS/ml}$  measured in 10, 20, 30, 40, 50 and 60 minutes were 0.226, 0.229, 0.231, 0.231, 0.230 and 0.234, respectively.

#### Stability of Solutions A–D

The data of calibration lines measured for fresh solutions A and D and for the same solutions measured 2 h (A) or 24 h (D) later are given in Tables II and III, respectively. (The remaining reagents were prepared immediately before each series of measurements.)

TABLE I  
Dependence of absorbance on DMDS concentration

$\rho_{\text{DMDS}}, \mu\text{g ml}^{-1}$	$A_{605}$
0.62	0.018
0.92	0.032
1.23	0.045
1.54	0.062
1.85	0.079
2.16	0.095
2.46	0.106
2.77	0.122
3.08	0.131
3.39	0.144
3.70	0.156

TABLE II  
Stability of solution A<sup>a</sup>

$\rho_{\text{DMDS}}, \mu\text{g ml}^{-1}$	$A_1$	$A_2$
3.27	0.140	0.091
3.79	0.162	0.111
4.37	0.187	0.136
4.98	0.213	0.163
5.52	0.236	0.187

<sup>a</sup>  $A_1$  absorbance for freshly prepared solution A,  $A_2$  absorbance after 2 h.

For solutions B and C prepared immediately before measurements and the same solutions stored for one month, the calibration lines were identical.

### Effect of Selected Volatile Substances Present in Gas Emissions from Rubber Plants on the Results of Determination of DMDS

Solutions containing mixtures of the standard solution of DMDS and the substance under investigation (quantities from 0.001 to 10 mg) were fed into the reduction column. The procedure of determination was the same as when measuring the calibration line. The results are given in Table IV. The effect of benzene (and/or toluene) (Table V) can be eliminated by adding the interferent (maximum amounts determined in the examined samples) to the calibration solutions.

TABLE III  
Stability of solution D<sup>a</sup>

$\rho_{\text{DMDS}}, \mu\text{g ml}^{-1}$	$A_1$	$A_2$
3.27	0.140	0.169
3.79	0.162	0.192
4.37	0.187	0.219
4.98	0.213	0.245
5.52	0.236	0.266

<sup>a</sup>  $A_1$  absorbance for freshly prepared solution D,  $A_2$  absorbance after 24 h.

TABLE IV  
Effect of selected volatile substances on the results of determination of DMDS

Compound	Effect	Absorbing substance
$\text{CH}_3\text{SH}$	overstated results	NaOH
$\text{H}_2\text{S}$	HgS precipitation	NaOH
$\text{SO}_2$	HgS precipitation	NaOH
$\text{NO}_2$	overstated results	NaOH
$\text{NH}_3$	overstated results	$\text{H}_2\text{SO}_4$
$\text{C}_6\text{H}_6$	lowered results	
$\text{C}_6\text{H}_5\text{CH}_3$	lowered results	
$\text{C}_6\text{H}_5\text{NH}_2$	overstated results	$\text{H}_2\text{SO}_4$
HCHO	overstated results	water

## Determination of DMDS in Gas Emissions from the Rubber Industry

*Sampling of air.* Air (20 l) was passed at a flow rate of 20 l/h through washers with solutions absorbing the interfering substances and then through two washers connected in series and containing 10 ml of methanol each.

*Determination.* The solutions from the washers with methanol were transferred to 10 ml volumetric flasks and diluted with methanol to volume. Either solution was analyzed separately. A 5 ml aliquot was placed in the reduction column, 2 ml of 1 M  $\text{H}_2\text{SO}_4$  were added and the column was closed. After 5 min, the solution was transferred to a 50 ml volumetric flask containing 5 ml of solution A. The column was washed with  $2 \times 5$  ml of 0.25 M  $\text{H}_2\text{SO}_4$  and the acid was added to the same flask. One ml of solution B was added, the whole was stirred for 30 s, and 10 ml of solution C were added and the system was diluted to volume with solution D. In 30 min, the absorbance of the solution was measured at 605 nm against a reagent blank.

The mass concentration of dimethyl disulfide in gas was calculated as

$$\rho_g = \frac{\rho_s 50V_1}{V_2V_g} \quad [\text{mg/m}^3], \quad (I)$$

where  $\rho_s$  is the found DMDS concentration in  $\mu\text{g/ml}$ , 50 is the volume of the volumetric flask in ml,  $V_1$  is the total volume of the absorbing solution in ml,  $V_2$  is the total volume of solution taken for determination in ml, and  $V_g$  is the volume of air sampled in l.

## RESULTS AND DISCUSSION

The results give evidence that the spectrophotometric method for the determination of mercaptans reported in literature<sup>1</sup> can be modified for organic disulfides as well. The

TABLE V  
Effect of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{H}_5\text{CH}_3$  on the results of determination of DMDS

Introduced			Determined	
$m_{\text{DMDS}}, \mu\text{g}$	$m_{\text{C}_6\text{H}_6}, \mu\text{g}$	$m_{\text{C}_6\text{H}_5\text{CH}_3}, \text{mg}$	$m_{\text{DMDS}}, \mu\text{g}$	Error, %
28.64	0	0	28.13	-1.8
	0	0	28.35	-1.0
	0.264 <sup>a</sup>	0	14.41	-49.7
	2.64	0	14.82	-48.2
	0	0.63 <sup>a</sup>	17.66	-38.3
	0	6.33	18.48	-35.5

<sup>a</sup> Maximum amount of the substance determined in the air samples.

reduction of dimethyl disulfide to mercaptan is carried out in a column filled with zinc amalgam. Attempts at plotting a calibration line according to the procedure given in literature failed to yield reproducible results. A number of experiments were performed to establish the optimum conditions for the analysis. As a result, it was found that the absorbance of the azo compound should be measured within 20–50 min from the colour reaction. Furthermore, it was found that:

- the mixture of  $\text{NaNO}_2$  and  $\text{H}_2\text{SO}_4$  is very unstable: in two hours after preparation of solution A the absorbance of the examined solutions decreased considerably, resulting in negative errors ( $\leq 30\%$ ) of determination of DMDS; hence, solution A should be prepared immediately before the measurements;

- the solution of *N*-(1-naphthyl)ethylenediamine dihydrochloride stored for 24 h causes an increase in the absorbance of the solutions examined (the results of DMDS determination are 10–15% overstated); this may be due to absorption of nitrogen dioxide from air in solution D; solution D should be prepared on the day the measurements are made;

- the mixture of  $\text{HgCl}_2$  and sulfanilic acid (solution B) and the solution of amidosulfonic acid (solution C) are stable for a minimum of one month.

Our investigations resulted in modifications to improve the precision and reproducibility of the method. The determination limit is  $0.6 \mu\text{g DMDS/ml}$  (relative error  $\leq 5\%$ ). The calibration line consists of two linear segments: 1) within the range of  $0.6$  to  $1.2 \mu\text{g DMDS/ml}$ ; and 2) at concentrations higher than  $1.2 \mu\text{g DMDS/ml}$ . In the sampling and measurement conditions applied, the determination limit of the spectrophotometric method is  $1.5 \text{ mg DMDS in } 1 \text{ m}^3$  of air. The relative standard deviation for a series of 8 measurements was  $0.85\%$ , and the confidence interval at 95% probability was  $3.08 \pm 0.02 \mu\text{g DMDS/ml}$ .

The method was applied to the determination of organic disulfides at workplace and in air pollutants from the rubber industry. The influence of some substances present in the gas emissions on the determination of disulfides by the spectrophotometric method was examined. A method was proposed to remove the interfering substances from the air sample (Table IV).

The method developed can be used to determine disulfides along with mercaptans when  $\text{NO}_2$  is absent ( $\text{SO}_2$  is absorbed in  $\text{NaHCO}_3$  (ref.<sup>4</sup>), and  $\text{H}_2\text{S}$  on an arsenic filter<sup>5</sup>), making two determinations simultaneously: mercaptans in the non-reduced sample and the sum of mercaptans and disulfide in the reduced sample.

The method developed was also used for the determination of DMDS in gaseous products of thermal decomposition of selected raw materials and intermediate products used in the rubber industry.

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