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Talanta 66 (2005) 125–129

Talanta

www.elsevier.com/locate/talanta

# Determination of methanol in *o,o*-dimethyldithiophosphoric acid (DMDTPA) of technical grade by UV/vis spectrophotometry and by HPLC

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Received 9 September 2004; received in revised form 11 October 2004; accepted 21 October 2004
Available online 8 December 2004

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## Abstract

Two procedures are proposed in this work for the determination of methanol impurities in *o,o*-dimethyldithiophosphoric acid (DMDTPA). To avoid possible interferences from the main component, DMDTPA was precipitated in the form of insoluble lead complex. Free Pb(II) ions were eliminated with sulfuric acid and methanol was oxidized to formaldehyde with potassium permanganate in methanesulfonic acid medium. Finally, the excess of oxidizing agent was neutralized with saturated sodium oxalate. The above pretreatment procedure was identical for spectrophotometric assay and for chromatographic determination. In the first case, the solution obtained was treated with Nash reagent to form 3,5-diacetyl-1,4-dihydrolutidine ($\lambda_{max} = 415$ nm). In the calibration range 0.1–1.0% (methanol in DMDTPA), the analytical figures of merit were: $R^2 = 0.9993$, quantification limit 0.02% methanol in DMDTPA coefficient of variance ($n = 5$) for 0.1% and 0.4% methanol respectively 6.7% and 2.4%. Recoveries obtained in the sample fortified with 0.1, 0.2, 0.4% of methanol (in DMDTPA) were in the range 99–105%. For chromatographic procedure, formaldehyde was derivatized with 2,4-dinitrophenylhydrazine and separation was achieved on Luna C18(2) column using the isocratic elution with acetonitrile–water (70:30, v/v) and spectrophotometric detection at 360 nm. In the calibration range 0.05–0.25% (methanol in DMDTPA), $R^2$ was always higher than 0.999, the quantification limit was 0.004% and the recoveries in these same fortified samples in the range 98–101%. No statistically significant differences were observed between the results obtained in the analysis of technical grade DMDTPA by the two procedures (ANOVA, $p < 0.05$)

*Keywords:* Methanol; *o,o*-Dimethyldithiophosphoric acid; UV/vis spectrophotometry; HPLC

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## 1. Introduction

*o,o*-Dialkyldithiophosphoric acids are widely used in the production of pesticides, lubricant additives and plastic stabilizers [1]. For quality control of technical *o,o*-dimethyldithiophosphoric acid (DMDTPA), the determination of methanol impurities is an important issue. Different analytical methodologies have been proposed for methanol determination, including spectrometric procedures in UV/vis [2–4] or infra-red region [5] and gas chromatography [6–8]. Usually, spectrophotometric procedures involve enzymatic reactions [9,10] or oxidation of methanol to formaldehyde [2,3]. Recently, few applications of high-performance liquid chromatography have also been reported. Thus, Chen et al. [11] used 3-bromomethyl-7-methoxy-1,4-benzoxazin-2-one for analyte derivatization and Zegota [12] separated the condensation product obtained from formaldehyde and 2,4-dinitrophenylhydrazine.

Since DMDTPA decomposes easily with formation of methanol (at elevated temperature, varying pH of medium, etc.), it has to be removed from the sample prior to methanol determination. On the other hand, several analytical applications of *o,o*-dialkyldithiophosphoric acids

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doi:10.1016/j.talanta.2004.10.008

have been reported in the literature, based on the formation of stable, non-polar complexes with metal ions. Jimenez de Blas et al. [13] used bismuth for indirect determination of dimethoxydithiophosphate by atomic absorption spectrometry after extraction of the stable complex to organic phase. Other authors used diethyldithiophosphate acid for enrichment and reversed-phase liquid chromatographic separation of respective arsenic (III), bismuth (III) and antimony (III) complexes [14]. Sasaki et al. [15] reported the application of weak diethyldithiophosphate complex with nickel for the extraction of metal ions via ligand exchange and they observed the following displacement order: palladium (II) > gold (III) > copper (I) > mercury (II) > silver (I) > copper (II) > antimony (III) > bismuth (III) > lead (II) > cadmium (II) > zinc (II).

In this work, a clean-up procedure has been proposed for the determination of methanol in dimethyldithiophosphoric acid, based on the precipitation of DMDTPA complex with metal ions. In the supernatant obtained, oxidation of methanol was carried out and formaldehyde was quantified by spectrophotometry with Nash reagent [2] or by reversed phase high-performance chromatography after condensation with 2,4-dinitrophenylhydrazine [12].

## 2. Experimental

### 2.1. Apparatus

A Milton Roy (Rochester, NY, USA) Spectronic 3000 Diode Array spectrophotometer with 0.35 nm resolution was used, coupled to a 486 PC and User data Version 2.01 (Milton Roy) software for spectral data acquisition, storage and manipulation. Absorption spectra were registered using quartz ultra-micro spectrophotometer cuvette, minimum volume 100 μl (Sigma).

A Hewlett-Packard (Waldbronn, Germany) Series 1050 high-performance liquid chromatograph with a multiple wavelength spectophotometric detector and ChemStation was used. A Phenomenex Luna C18(2) column (5 μm, 250 mm × 4.6 mm) was used at room temperature.

### 2.2. Reagents

The solvents were of HPLC-grade quality and all other chemicals were of analytical-reagent grade.

A stock standard solution of methanol 0.5% (v/v) (Fisher) was used. The aqueous solutions of lead acetate (saturated, about 10%), potassium permanganate (2%), sodium oxalate (saturated), sulfuric acid (1 mol $l^{-1}$), methanesulfonic acid (1 mol $l^{-1}$) and Nash reagent (4 mol $l^{-1}$ ammonium acetate, 50 mol $l^{-1}$ acetic acid, 20 mol $l^{-1}$ acetylacetone) were prepared from Sigma reagents.

2,4-Dinitrophenylhydrazine (DNPH) 3.5 mol $l^{-1}$ in hydrochloric acid, 2 mol $l^{-1}$ (purified by two extractions with hexane) was used as the derivatization agent in chromatographic procedure.

Acetonitrile and hexane were from Fisher, acetylacetone from Merck.

Deionized water (Labconco, USA) was used throughout.

Purified, methanol-free standard of *o,o*-dimethyldithiophosphoric acid and the technical product were from Tekchem, S.A. de C.V.

### 2.3. Procedures

#### 2.3.1. Separation of DMDTPA and oxidation of methanol

The aliquot of technical product (50 μl) was diluted 1:1 with deionized water in the Eppendorff tube. The precipitation of DMDTPA was accomplished by addition of lead acetate solution (700 μl) and the sample was centrifuged (5 min, 5000 × *g*). A volume of supernatant (100 μl) was transferred to a new plastic tube, 100 μl of 1 mol $l^{-1}$ sulfuric acid was added and, again, the sample was agitated (vortex) and centrifuged (2 min, 3000 × *g*). The oxidizing mixture (20 μl potassium permanganate, 2% and 100 μl methanesulfonic acid, 1 mol $l^{-1}$) was added to 25 μl of supernatant and the mixture was left for 2 min. To stop the oxidation reaction, 20 μl of saturated solution of sodium oxalate were added to the tube (color disappeared in about 15 s).

Once the main compound (DMDTPA) was eliminated and methanol converted to formaldehyde, this same solution was used in both spectrophotometric and chromatographic procedures.

#### 2.3.2. Spectrophotometric determination

A series of calibration solutions were prepared by mixing 50 μl of the appropriate methanol standard solution with 50 μl of methanol-free DMDTPA, thus covering analyte concentrations 0, 0.2, 0.4, 0.6, 0.8, 1.0% (v/v in methanol-free DMDTPA). Methanol oxidation was carried out as described above. The Nash reagent (500 μl) was then added to the solutions obtained and the mixtures were kept at 60 °C during 10 min. After cooling to room temperature, the absorbance was measured at 415 nm. The quantification in technical-grade DMDTPA was carried out by external calibration and by standard addition method (0.1, 0.2, 0.4% (v/v) of methanol). Three replicates were carried out and blank was run in parallel.

#### 2.3.3. HPLC procedure

The oxidation of methanol to formaldehyde was carried out as described above. The calibration solutions contained 0, 0.05, 0.10, 0.15, 0.20, 0.25% (v/v) of methanol in methanol-free DMDTPA and were processed using this same procedure (2.3.1). The derivatization of formaldehyde with 2,4-dinitrophenylhydrazine was carried out. To do so, after clean-up procedure and methanol conversion to formaldehyde, 500 μl of 2,4-DNPH, 3.5 mol $l^{-1}$ in 2 mol $l^{-1}$ hydrochloric acid were added to the samples and to the calibration solutions. After incubation (10 min, room temperature), the respective dinitrophenylhydrazone was extracted with hexane (3 × 500 μl), the solvent was evaporated in the nitrogen stream and residue dissolved in 200 μl of acetonitrile. The solution obtained (20 μl) was injected to the chromatographic system and isocratic elution with acetonitrile:water (70:30, v/v) was performed using a flow rate 1.0 mol $l^{-1}$. Detection was carried out at 360 nm (ref. 550 nm).

## 3. Results and discussion

When a technical product is to be analyzed for trace impurities, sample pretreatment becomes necessary in order to avoid possible matrix interferences. In this work, the determination of methanol in DMDTPA has been undertaken. Since methanol is formed during the decomposition of the main compound, the latter had to be removed before the analysis. The original idea was to eliminate DMDTPA through its precipitation in form of water-insoluble metal complex. In the supernatant obtained, methanol was oxidized to formaldehyde. The aliquots of such prepared samples were taken for spectrophotometric assay and for chromatographic analysis. Nash reagent and 2,4-dinitrophenylhydrazine were the respective derivatization agents. The clean-up procedure and derivatization reactions were performed using small volumes (total) volume of the sample and reagents mixture below 1.5 ml). The sample volume was set at 50 μl (about 0.25 mol $l^{-1}$ DMDTPA), the volumes and concentrations of reagents were selected experimentally to fit within a calibration range 0.05–1% of methanol in DMDTPA.

In the first approach, the effect of different metal ions on the precipitation of DMDTPA was examined. The standard of DMDTPA (50 μl, methanol-free) was diluted twice with deionized water and 0.5 ml of the solution containing about 0.5 mmol of lead acetate, zinc nitrate, copper nitrate, bismuth nitrate or antimony nitrate was added. In each case, the formation of precipitate was observed. To compare the efficiency of metal ions in DMDTPA precipitation, the acidified solution of potassium permanganate was added (drop by drop) to the supernatant. The disappearance of color was observed, due to permanganate reduction by DMDTPA (thiol groups). Minimum volume of permanganate used to obtain colored solution was taken as the criterion to compare the efficiency of DMDTPA precipitation in the presence of the ions mentioned above. From the results obtained, lead acetate was selected for further experiments. Similarly, the volume of Pb(II) solution was selected (drop by drop addition of lead acetate and permanganate test). To avoid possible interferences during oxidation of methanol or during derivatization reactions, the excess of metal ions was precipitated with sulfuric acid (see section 2.3).

The experimental conditions appropriate for oxidation of methanol to formaldehyde were studied using 0.6% methanol in DMDTPA standard. After elimination of DMDTPA and the excess of Pb(II), acidified potassium permanganate was used as the oxidation agent [4,10,11]. The amount of potassium permanganate was selected to assure its molar excess with respect to 1% methanol in DMDTPA (see section 2.3). The key point in the experimental development was to avoid further oxidation of formaldehyde. Three different acids were used for sample acidification and the analytical signal was monitored during 5 min. This signal was measured as absorbance at 415 nm, after formaldehyde had been derivatized with Nash reagent [2,4,16]. In Fig. 1, the effect of sulfuric, methanesulfonic and phosphoric acids on the analytical signal at different reaction times is presented. Similar rates of formaldehyde formation can be observed in the presence of methanesulfonic and sulfuric acids. However, in the latter case the signal decreased significantly after 1 min (formaldehyde oxidation). In the presence of phosphoric acid, the kinetics of formaldehyde formation was less favorable and the analytical signal lowered with the increasing time of oxidation. Different concentrations of methanesulfonic acid were tested and the results are presented in Fig. 2. As can be observed, the highest signal was obtained in the presence of 1.0 mol $l^{-1}$ methanesulfonic acid and this signal was rela-

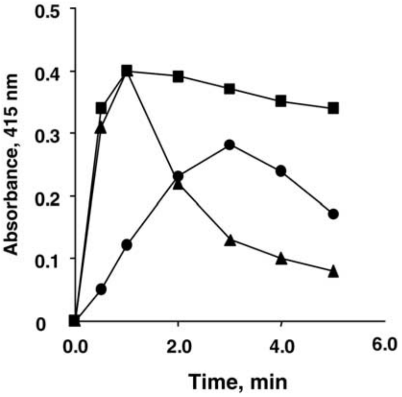

Fig. 1. Effect of different acid media (1 mol $l^{-1}$) used for methanol oxidation on the analytical signal of 0.6% methanol in DMDTPA (signal measured after derivatization of formaldehyde with Nash reagent): (■) methanesulfonic acid; (▲) sulfuric acid; (●) phosphoric acid.

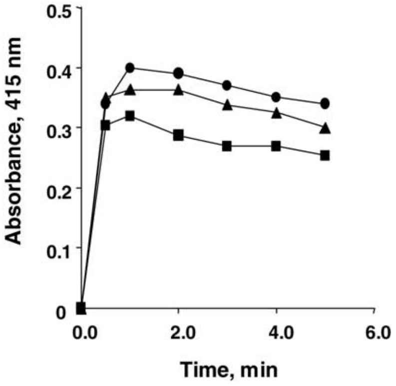

Fig. 2. Effect of the concentration of methanesulfonic acid on the analytical signal of 0.6% methanol in DMDTPA (measured after derivatization of formaldehyde with Nash reagent): (▲) 0.5 mol $l^{-1}$; (●) 1.0 mol $l^{-1}$; (■) 1.5 mol $l^{-1}$.

Table 1
Analytical figures of merit evaluated for the proposed spectrophotometric procedure

| Parameter | |
|---|---|
| Linear regression equation | $A_{415\mathrm{nm}} = 0.550\ c_{\mathrm{MeOH}} + 3.6 \times 10^{-3}$ |
| $R^2$ | 0.9993 |
| Standard error for intercept | $5.2 \times 10^{-4}$ |
| Standard error for slope | $8.58 \times 10^{-3}$ |
| QL, (%) | 0.02 |
| CV for 0.1% methanol in DMDTPA | 6.7 |
| CV for 0.4% methanol in DMDTPA | 2.4 |
| Recovery in the fortified samples ($n = 3$), (%) | |
| 0.1 methanol | $105 \pm 4$ |
| 0.2 methanol | $101 \pm 3$ |
| 0.4 methanol | $99 \pm 2$ |

$C_{\mathrm{MeOH}}$—methanol concentration in DMDTPA, %; QL—quantification limit given as % of methanol in DMDTPA; CV—variance coefficient ($n = 5$).

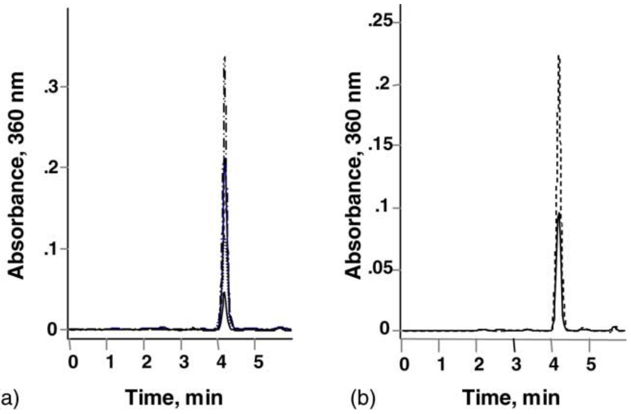

Fig. 3. Typical reversed phase chromatograms: (a) calibration samples: (—) 0.05%; (······) 0.10%; (- - - -) 0.15% y (-·-·-·-) 0.20% of methanol in DMDTPA (b) (—) DMDTPA of technical grade and (- - - -) this same sample spiked with 0.10% of methanol.

Table 2
Comparison of the analytical results obtained in the determination of methanol by the two procedures proposed in this work

| Sample | Methanol concentration in technical DMDTPA, % ±S.D. | |
|---|---|---|
| | Spectrophotometry | HPLC |
| 1 | $0.08 \pm 0.01$ | $0.078 \pm 0.004$ |
| 2 | $0.14 \pm 0.01$ | $0.146 \pm 0.003$ |
| 3 | $0.37 \pm 0.02$ | $0.374 \pm 0.009$ |

tively stable for the reaction time between 1 and 3 min. To stop the oxidation reaction (after 2 min), permanganate excess was reduced with sodium oxalate, sodium nitrite, hydrogen peroxide and sodium arsenite, as described in earlier reports [2,4,10,11,16]. In the presence of sodium nitrite or sodium oxalate, we observed almost instant disappearance of color. Saturated sodium oxalate was though selected for further studies, in order to avoid possible interferences of nitrite in derivatization reaction with 2,4-DNPH.

Once the experimental conditions for clean-up procedure and for methanol oxidation had been established, the derivatization procedure with Nash reagent was applied and the spectrophotometric measurements carried out (see procedures). Owing to the acidity of the solution, the concentration of ammonium acetate was increased with respect to that typically used in Nash reagent (4 mol $l^{-1}$ instead of 2 mol $l^{-1}$) [4,9,16]. Analytical figures of merit, evaluated within the calibration range 0.1–1.0% of methanol (v/v in methanol-free DMDTPA) are given in Table 1. The limit of quantification expressed as the % of methanol in DMDTPA was 0.02%, which corresponds to 5 $\mu$mol $l^{-1}$ of analyte in the final solution, in agreement with values reported for other spectrophotometric procedures [4,9,10]. For accuracy checking, the recovery experiments were carried out, using three levels of methanol addition (0.1, 0.2 and 0.4%). As can be observed in Table 1, the obtained values were in the range 99–105% confirming the feasibility of the procedure for methanol determination in DMDTPA of technical grade.

This same pretreatment protocol (precipitation of DMDTPA and methanol oxidation) was also used for liquid chromatographic determination of methanol. The precolumn derivatization of formaldehyde was carried out with 2,4-dinitrophenylhydrazine in acid medium, as described elsewhere [17]. The reversed phase chromatographic separation was performed with acetonitrile–water (70:30, v/v). Using a flow rate 1.0 ml $\mathrm{min}^{-1}$ and the spectrophotometric detection at 360 nm, the elution of target compound was observed at 4.23 min (Fig. 3a). The calibration was performed within the concentration range 0.05–0.25% of methanol in DMDTPA. The linear regression equation for peak area measurements (PA) was $\mathrm{PA} = 1.81 \times 10^4\ c_{\mathrm{MeOH}} + 22$, regression coefficient was always >0.999, relative standard error of the slope and intercept respectively 2% and 30%, the limit of quantification 0.004% methanol in DMDTPA and the coefficients of variance at two levels of methanol in DMDTPA (0.05% and 0.20%), respectively, 2.3% and 1.1%. The DMDTPA was fortified with 0.05, 0.10 and 0.20% of methanol (as impurity in DMDTPA) and the recoveries obtained were $100.8 \pm 0.9\%$, $98.7 \pm 1.1\%$ and $99.7 \pm 0.4\%$, indicating acceptable accuracy of the determination.

Finally, the analysis of three DMDTPA samples of technical grade was carried out using the two procedures proposed in this work. The method of standard addition was used for quantification. In Fig. 3b, typical chromatogram of the sample and the spiked sample are presented. The analytical results are presented in Table 2, indicating a good agreement between the results of the two procedures (ANOVA, $p < 0.05$).

## 4. Conclusions

Two micro scale procedures are proposed in this work for the determination of methanol in technical DMDTPA. The clean-up, based on the precipitation of DMDTPA in form of its complex with lead ions and the conversion of methanol to formaldehyde are the common steps prior to spectrophotometric assay and to chromatographic analysis. The analytical results obtained indicated feasibility of the two approaches for the determination of methanol in industrial product. The advantage of spectrophotometric assay relies on its simplicity, no need for sophisticated instrumentation, low cost, short time of analysis and, in consequence easy application in routine analysis. Since the chromatographic procedure provides better sensitivity, this is more suitable for the determination of methanol at lower concentrations.

## Acknowledgements

The authors gratefully acknowledge financial support from CONCyTEC (Guanajauato, Mexico), project number 0016-201-056 and TEKCHEM, S.A. de C.V. (Salamanca, Mexico). The authors acknowledge TEKCHEM, S.A. de C.V. for providing DMDTPA standard and the samples of technical product.

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