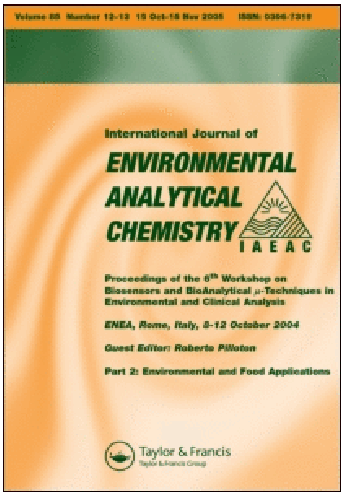

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# Gas Chromatographic Determination of O-Ethyl S-(N, N-Diisopropylamino) Ethyl Methylphosphonothiolate and O, O-Diisopropyl S-Benzyl Phosphorothiolate as Corresponding Phosphonofluoridate and Phosphorofluoridate

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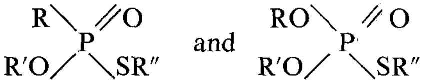
A gas chromatographic method has been reported for the determination of phosphonothiolates and phosphorothiolates as corresponding phosphonofluoridates and phosphorofluoridates after reaction with AgF. The transformation reaction procedures and the chromatographic conditions were recommended for the model compounds, O-ethyl S-(N, N-diisopropylamino)ethyl methylphosphonothiolate (MESP) and O, O-diisopropyl S-benzyl phosphorothiolate (DPSP). The results obtained have shown that the recovery is 100 ± 4.5% for determination of MESP in the range of 1.88–8.00 μg/ml (in benzene solution) and the relative standard deviations (RSD) are less than 2.12% for MESP and DPSP at the 3.18, 6.30 and 5.48 μg/ml level.

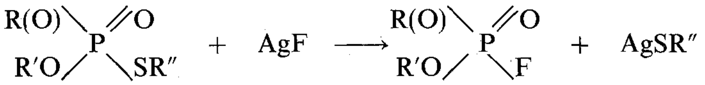
## INTRODUCTION

Phosphonothiolate and phosphorothiolate compounds



are often used as pesticides and germicides. A few of them are also used for warfare agents.[1,2] These compounds usually have higher boiling points and most of them are unstable at high temperature. In order to obtain reasonable retention time in gas chromatography, the non-polar columns with the low content of stationary phase must be used to increase the chance of reaction of the compound with the carrier. But the determination sensitivity will be greatly reduced and the micro-determination of these compounds by gas chromatography is difficult.[3] For example, in our previous experiment[4] using the column packing with ethylene glucol succinate for analyzing MESP in benzene by gas chromatography, the lowest detectable concentration is only 30–50 $\mu$g/ml and for DPSP in benzene even 30 $\mu$g/ml is not attainable.

To resolve the problem of quantitative determination of these compounds in the range of low concentration (low $\mu$g/ml range) by gas chromatography, transformation of phosphonothiolates with AgF into the corresponding phosphonofluoridates[5,6] is carried out. The resulting products have greater volatility and much lower boiling points.



The phosphonofluoridates or phosphorofluoridates are determined with alkali flame ionization detector (AFID) gas chromatography with high sensitivity. In the study of the methods of transformation and determination of MESP and DPSP in benzene, two species cited were used as model compounds.

## EXPERIMENTAL

### Apparatus and reagents

A Model 103 gas chromatograph with AFID (Analytic Instrument Factory of Shanghai) was used.

Polyethylene powder (PP) is in the shape of cotton. Paper of polyperchloroethylene (PPC) and cloth of polyester fibre without spinning (CPF) were cut into a size of about 10 mm$^2$ (Chemical Plant of Lanzhou). Model I filter paper (FP) (made in Filter Paper Plant of Hangzhou Xinhua), has characteristics similar to No. I Whatman. MESP and DPSP were synthesized with reference to U.S. Pat. 3903210 and previous literature,[7] and distilled before use.

Silver fluoride. 12.5 gm sodium fluoride is dissolved in 500 ml of hot-deionized water. Then 37.0 gm potassium fluoride is added to it and 66.5 gm of silver nitrate is added slowly under stiring. About 250 gm of PP (or PPC, CPF and FP) is taken and immersed in an amount of 95% ethanol for a few minutes. Filtrate the mixture through a funnel under pumping to remove the ethanol as completely as possible. After standing of the silver fluoride solution for 30 minutes, pour the upper clear solution to the immersed PP and stir it. The mixture is dried in an oven at $50 \pm 1$°C. The greyish powder obtained is stored in a plastic bottle, protected from light. It can be used for a few years.

### Procedure of the transformation

The transformation reagent, silver fluoride, is filled into a short titrating tube (see Figure 1). Opening up the cock of the tube, the benzene solution containing a sample and benzyl chloride (internal standard) is poured slowly into the transformation tube from the top. When the bottom of the tube is soaked with the solution the cock is switched off and some of the benzene solution is poured further with the result that the transformation reagent is immersed completely. To prevent the solvent from loss by volatilization the transformation tube is closed with a rubber stopper. After standing for 20 minutes, the solution is squeezed into a pointed bottom small test tube with a bulb ear washer for application to the chromatographic determination.

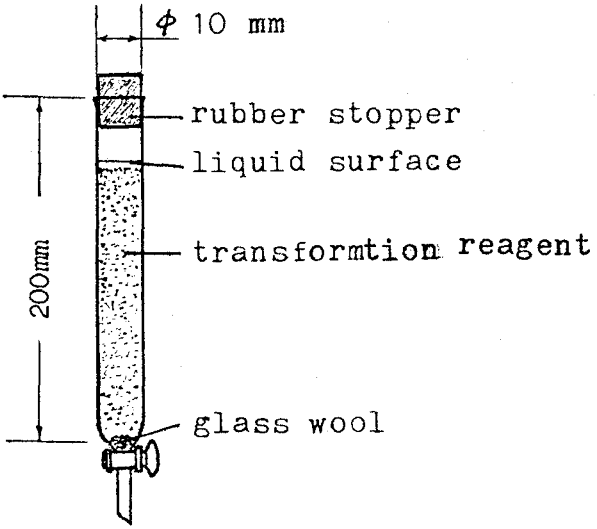


FIGURE 1 Transformation tube.

## Determination of MESP

A certain amount of sample weighed accurately is dissolved into the benzene solution containing 2.4 mg/ml benzyl chloride to prepare a series of calibrated concentration solution and is transformed according to the method described.

The conditions of chromatographic analysis are: the teflon columns (200 × 2 mm I.D.) were packed with 10% ethylene glucol succinate on 80–100 mesh 101 white silanized support, the temperatures of column, injector and AFID were 120, 240 and 220°C respectively, the flow-rate of carrier gas (hydrogen) was 30 ml/min, air 400 ml/min.

One microliter of each of a series of transformed calibration samples is injected into the chromatographic injector and a chromatogram is obtained (Figure 2). In the experiment to construct the standard curve for determination MESP it was demostrated that linearity range at least is 2–20 $\mu$g/ml and regression coefficient is 0.135.

### Determination of DPSP

Except for chromatographic conditions, the remaining procedures are the same as for MESP.

The chromatographic conditions are as follows. The teflon (200 × mm I.D.) were packed with 7% ethylene glucol succinate on 80–100 mesh 101 white silanized support; the temperatures of column, injector and AFID were 120, 180 and 160°C respectively; the flow-rate of carrier gas (nitrogen) was 15 ml/min, air 360 ml/min and hydrogen 27 ml/min.

## RESULTS AND DISCUSSION

### Recovery and reproducibility of the determination

The results in Table I show that the MESP tested for quantitative determinations is in the range 1.88–8.00 μg/ml with recoveries of 100 ± 4.5%. As long as the conditions for the transformation and chromatographic operation remained same a better reproducibility was obtained. The data in Table II also show that the RSD is less than 2.12% for MESP at the 3.18, 6.30 and 5.48 μg/ml level.

### Support for transformation reagent

There is already a known method for phosphonothiolate compounds to be transformed into phosphonofluoridates in an aqueous

TABLE I

Results of MESP in benzene

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Prepared concen. (μg/ml) | 1.88 | 2.00 | 2.50 | 3.18 | 3.50 | 4.00 | 5.00 | 6.36 | 8.00 |
| Determined Concen. (μg/ml) | 1.90 | 2.09 | 2.60 | 3.31 | 3.36 | 3.94 | 5.14 | 6.16 | 7.80 |
| Recovery (%) | 101.1 | 104.5 | 104.0 | 104.1 | 96.0 | 97.5 | 102.8 | 96.9 | 97.5 |

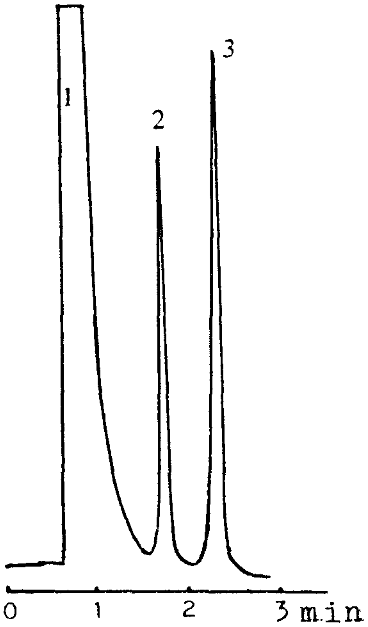


FIGURE 2 A chromatogram of MESP in benzene. Sample 6.0 μg/ml, injection volume 1 μl. (1) Benzene, (2) internal standard and (3) sample.

TABLE II
Reproducibility of determination results for MESP and DPSP in benzene

| Sample | MESP | | DPSP |
|---|---|---|---|
| Prepared concen. (μg/ml) | 3.18 | 6.30 | 5.48 |
| Determined mean (μg/ml) | 3.31 | 6.19 | 5.46 |
| Number of times | 5 | 5 | 5 |
| RSD (%) | 0.71 | 0.75 | 2.12 |

solution,[5,6] but this method can not be used for chromatographic analysis because AgF is insoluble in organic solvents. We adsorbed the AgF to the surface of a support to increase the chances of contact of AgF with the phosphonothiolates or phosphorothiolates in organic solvent for complete transformation. PPC, CPF and FP

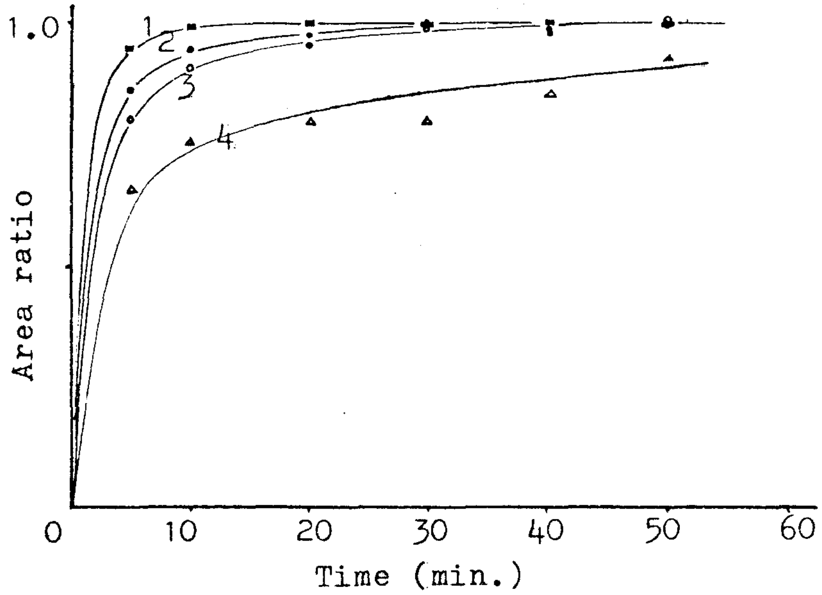


FIGURE 3 Time dependence of the MEFP formation. Sample: MESP, 6 μg/ml (in benzene); Reagent AgF on support. Area ratios given compare sample to the internal standard (benzyl chloride). Support: (1) PP, (2) CPF, (3) FP and (4) PPC.

all can be used as support, but they were not better than PP. They were compared with respect to the time needed to transform MESP completely into O-ethyl S-(N,N-diisopropylamino)ethyl methylphosphonofluoridate (MEFP). It is found in Figure 3 that the time for complete transformation of MESP to MEFP using PP, CPF and FP were 20, 30 and 45 minutes respectively. As to PPC, the transformation can not be completed even in an hour. In addition, the materials reacting with AgF, such as silica gel, glass powder, quartz powder and so on, can not be used as supports for the transformation reagent.

## Acknowledgement

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