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Analysis of Methylisothiocyanate Derived from the Soil Fumigant Metham-Sodium in Workroom Air

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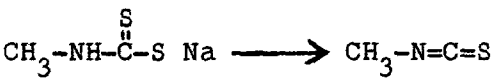
Metham-sodium (sodium N-methyl dithiocarbamate) is a soil fungicide, nematicide, and herbicide with a fumigant action. It is generally formulated as an aqueous solution containing 32.7% anhydrous sodium salt.

Its activity is due to decomposition to methyl isothiocyanate (MITC):



Methyl isothiocyanate, also called "methyl mustard oil" is a highly toxic and a powerful irritant product. Its vapours can be used as a military gas, too (SAX 1975). Therefore, any traces of the MITC vapours have to be monitored in the ambient air, during the manufacturing of metham-sodium, wherever this pesticide is bottled, as eventual release of MITC vapours could cause serious hazards to workers' health.

A simple analytical method was developed to quantitatively analyse MITC in workrooms' air by means of absorption of the gas in a solid support, desorption with solvent and subsequent gaschromatographic analysis.

As the sorbent column, we found very useful, inexpensive, and suitable, to use disposable, home made, small charcoal columns, instead of the porous polymeric materials like Chromosorb Century 101-108 series (Johns Manville Corp.), Porapak series (Weters Associated), Amberlite XAD-series (Rohm & Haas Chem. Co.) Tenax GC (Akzo BV, The Netherlands or Applied Science Laboratories Inc.), or polyurethane foams, now in general use as collection sorbents for organic pollutants in air (BIDLEMAN & OLNEY 1974, FARWELL *et al.*

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1977, PELLIZZARI et al. 1975 and 1976, THOMAS & SEIBER 1974).

We routinely use the same system for a monitoring program in the workrooms of our pesticide manufacturing plant, mainly analyzing: organophosphorous, organochlorine and thiocarbamate pesticides; solvents (xilenes, cyclohexanone, phenol); and fumigants (carbon tetrachloride, ethylene dichloride, dichloropropane, and dichloropropenes) (MAINI & COLLINA 1977).

The collection apparatus consist of a Pasteur pipette; filled with abt. 0.8 g activated charcoal granules, 1.5 mm (E.Merck, Darmstadt, GFR, Cat.no. 2514) held into the tube by glass wool plugs. This small column is connected by a rubber tubing to a Gelman EC-2000 apparatus (Gelman Instruments SpA, Opera-Milan, Italy), equipped with aspiration pump; timer; flow-, temperature-, and gas- meters. The collection air flow rate is 2-4 L/min, the time depending upon the concentration.

For the analysis, MITC is desorbed by shaking with 5 mL of CS_2 into a screw-cap test tube (Sovirel, France, Cat.no. 4.611-56).

Quali-quantitative determination of desorption solutions is carried out by GLC-FID (Varian Aerograph, mod. 1440). As the analytical column, we found particularly suitable a 180x0.3 cm i.d. pyrex glass column, packed with 0.2% Carbowax 1540 on Carbopack C, 80-100 mesh (Supelchem Srl, Milan).

These graphitized carbon black GC columns are particularly suitable for the analysis of volatile organics (SUPELCO INC. 1976, BRUNER et al. 1973, DI CORCIA et al. 1973, DI CORCIA & LIBERTI 1976, CICCIOLI et al. 1976, LEWIS et al. 1977).

Operating conditions are as follows: temperatures: 70°, 200°, and 210°C, respectively for the column oven, injector, and detector; gas flow rates: 24, 32, 150 mL/min, respectively for: N_2 carrier gas, hydrogen, and air.

The GC behavior of MITC, with the above operating conditions, is shown in Figure 1: the R_t is 2.8 minutes.

Attainable sensitivity GC level is 0.02 ug MITC standard in CS_2 solution.

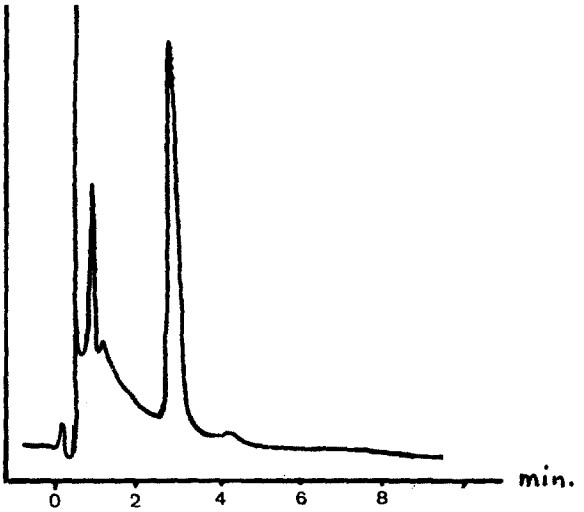

FIGURE 1 - Gaschromatogram of MITC on a 0.2% Carbo wax 1540/Carbopak C, 80-100, column (other conditions in the text)

The overall efficiency of the solid sorbent collection system was controlled by both collection and desorption recovery efficiencies.

Collection efficiency was tested by the method indicated by FARWELL et al. (1977) for 2,4-D esters volatile vapours in environmental air, using MITC standard (BDH Labs., Poole, England).

We reached a collection recovery of 92%, at a flow rate of 4 L/min, and a collection time of 2 hrs.; furthermore, it was found that a single charcoal column is sufficient.

Desorption efficiency was determined by analysis of CS_2 desorption solutions obtained from charcoal columns added with known amounts of MITC by microsyringe, and then submitted to air flowing.

It was found that desorption is the limitant step for recovery efficiency, because the collection in a single charcoal column is complete: the glass wood plug used for the collection efficiency, in fact, is absolutely free of MITC residues, as well as the second column. The cited control procedure (FARWELL et al. 1977) was applied also to aqueous solutions of metham-sodium (agricultural fumigant GEORT(R), containing 32.7% a.i.): 44, 160, and 586 mg of GEORT were sweeped-off for 8 hrs at 4 L/min.;

the charcoal columns trapped 1.11, 3.31, and 7.63 mf of MITC, respectively.

Both the collection with charcoal sorbent and the desorption procedure with CS_2, followed by GC determination, are well known and overall used as official methods for the determination of volatile organic contaminants in open and workrooms' air (COOPER et al. 1971, GROB & GROB 1971, WHITE et al. 1971, N.I.O.S.H. ANAL. METHODS 1975, VAN DYK & VISWEWARIAH 1975, HILL et al. 1976, Mc CAMMON 1976, MARIOTTI 1977). However, the novelty of the present method is the use of such techniques for the analysis of toxic vapours of fumigant methyl isothiocyanate, and the use of a Carbopak/Carbowax column for the GC analysis of this compound. A GC analysis of MITC residues in soil after metham-sodium application was developed by TURNER & GORDON (1963) using a 4% DC-550/Fluoropak 80 GC column.

It should be pointed out that, other than the metham-sodium, the dazomet (3,5-dimethyl tetrahydro-2-thio-1,3,5-thiadiazine) soil fumigant and fungicide, too, develops its activity by virtue of the release of the MITC vapours.

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