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DETERMINATION OF 3,3'-DICHLORO-4,4'-DIAMINODIPHENYLMETHANE IN AIR

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SUMMARY

A simple gas chromatographic method is described for the analysis of 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) in air. MOCA is quantitatively collected on a Gas-Chrom S tube and the solid sorbent is extracted with acetone. An aliquot sample of the extract is introduced directly into the gas chromatograph, using a microsyringe and the sample is chromatographed on a 1-ft., silylated 10% Dexsil column. The peak area of MOCA is measured and related to the concentration via a calibration curve prepared with a constant volume of standards. The chloroanilines associated with MOCA cause no interference; however, interference can be expected from any compounds having a retention time identical to that of MOCA. As little as 0.002 μg of MOCA per μl of acetone can be detected by this method.

INTRODUCTION

3,3'-Dichloro-4,4'-diaminodiphenylmethane (MOCA)*, an important curing agent for Adiprene polymer, has recently been classified as a carcinogen by the Occupational Safety and Health Administration[1]. As such, the working environment involved in the use and handling of this material must be monitored to ensure the safety of personnel. Because of our need to comply with this federal regulation, reliable methods were sought to sample and analyze MOCA in air.

Linch *et al.*[2] reported colorimetric and chromatographic methods for the analysis of MOCA. The colorimetric method proved to be difficult because interference from related compounds could not be readily eliminated. The gas chromatographic (GC) method, on the other hand, requires the conversion of MOCA to the corresponding trifluoroacetyl derivative prior to analysis. To achieve the reported sensitivity, slight modifications to this procedure were incorporated by Mehrhoff[3].

In considering the analytical aspects of MOCA, a direct analysis in which sample preparation is kept at a minimum would be a distinct advantage in the overall procedure. Stouder[4] developed a GC method, using an electron capture detector (ECD) with a 5-ft. 1.5% OV-17 column. Although this method is sensitive, a pre-

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* MOCA = Trade name of DuPont, Wilmington, Del., U.S.A.

vailing problem is the loss of standing current due to the contamination of the detector. In this article we describe a direct analysis of MOCA by flame ionization GC free from any detector problem and a solid sorbent tube for the collection of MOCA in air.

EQUIPMENT AND REAGENTS

An Aerograph HY FI Model 600-D gas chromatograph equipped with a flame ionization detector (FID) and a Varian Model A-25 recorder were used throughout this work. A ⅛-in.O.D. Pyrex injector liner was installed in the sample inlet.

A 1-ft. × ⅛-in.O.D. (0.094-in.I.D.) stainless-steel tube was packed with 10% by weight of Dexsil 300 GC coated on 80–90 mesh ABS Anakrom. The packed column was preconditioned at 300° for 24 h with helium at a flow-rate of 40–50 ml/min. Silylation of the packed column was accomplished by installing the column and the glass liner on the gas chromatograph. A column temperature of 150° and a helium flow-rate of 30 ml/min were maintained while introducing three 10-μl samples of Silyl-8 into the gas chromatograph with a Hamilton microsyringe. The detector was removed from the instrument to avoid contamination.

MOCA was purchased from Aldrich (Milwaukee, Wisc., U.S.A.). The compound was purified by thin-layer chromatography (TLC), and the purified sample had an indicated purity of 99.5% by elemental and TLC analyses.

Helium and ultrapure hydrogen were obtained from Matheson, Coleman and Bell (East Rutherford, N.J., U.S.A.) in H-size cylinders. Air was obtained from Los Alamos Scientific Laboratory Gas Facility prepared by mixing liquefied oxygen and nitrogen to 21% oxygen. All cylinders were equipped with pressure regulators and needle valves for flow controls.

AR-grade acetone and Silyl-8 were purchased from Mallinckrodt (St. Louis, Mo., U.S.A.) and Pierce (Rockford, Ill., U.S.A.), respectively.

Hamilton microsyringes (10-μl and 25-μl capacities), volumetric pipettes, and 1- and 10-ml volumetric flasks were used to transfer and contain the solutions.

A machinist ruler (50 divisions/in.) was required for area measurement.

Gas-Chrom S (40–60 mesh) purchased from Applied Science Labs. (State College, Pa., U.S.A.) was sieved to 45-mesh size and packed into a 2½-in. × ¼-in. O.D. tapered Pyrex tube as two separate sections, 10 and 50 mg. These sections were held in place with thin layers of quartz wool.

EXPERIMENTAL

The selection of a partitioning column to separate MOCA from the acetone solvent as a symmetrical peak with a reasonable retention time proved to be a problem. After screening a variety of columns, Dexsil 300 GC, a carborane-siloxane polymer, coated on 80–90-mesh ABS Anakrom met our requirements. By varying the amount of liquid phase from 5–20% by weight, drastic changes were observed on the chromatograms. With 5% Dexsil, a sharp and symmetrical peak was obtained for MOCA but the peak appeared on the steep, tailing edge of the acetone peak to make area measurement difficult. The 20% Dexsil column led to peak broadening due to an increase in the retention time. Hence, a 10% Dexsil column was considered the best compromise for our work.

The loss of MOCA was evident as the peak area decreased with continuous use of the column. To obviate this effect, a glass injector liner made of $\frac{1}{8}$-in.O.D. Pyrex tubing was inserted into the sample inlet of the gas chromatograph and flushed against the column inlet. The column length was reduced to 1 ft. and the column temperature was lowered to 200°. In addition, the interior walls of the glass liner, the column, and the detector base were silylated. After column stabilization, reproducible results were obtained.

The three gases used in this GC method greatly influence the detector response toward MOCA. For proper operation of the FID, the flow-rate of air was set at 350 ml/min. The helium flow-rate of 35 ml/min was based on the retention time and peak symmetry of MOCA, as determined from our earlier studies at a column temperature of 200° and inlet temperature of 265°. Using these conditions, the flow-rate of hydrogen was varied to determine the influence of this gas on the peak area of MOCA. Fig. 1 shows a graphic plot of the data.

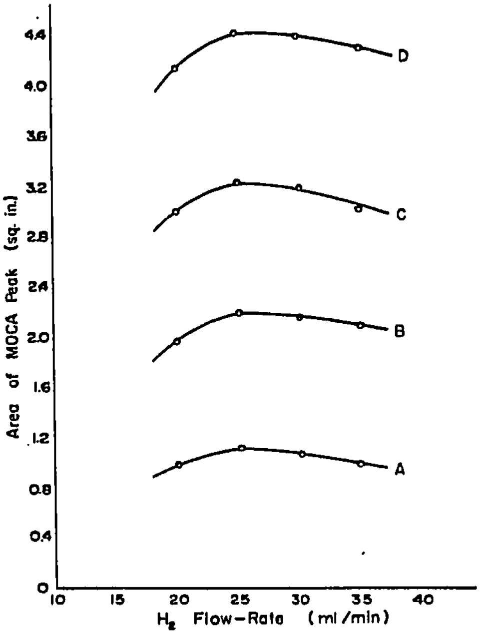
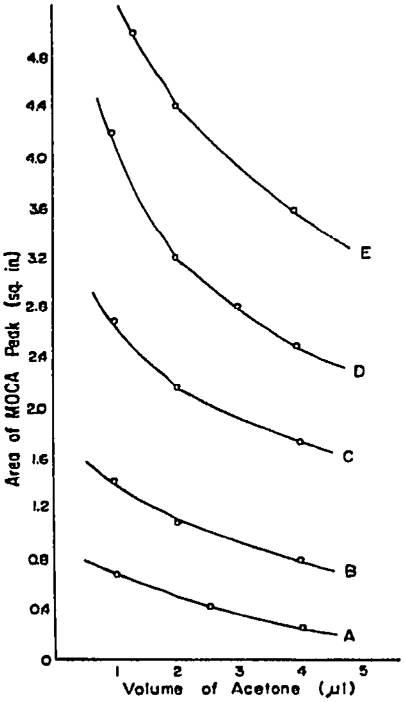


Fig. 1. Effect of hydrogen flow-rate on the peak area of MOCA. A = 0.050 μg MOCA; B = 0.100 μg MOCA; C = 0.150 μg MOCA; D = 0.200 μg MOCA.

It is obvious that an optimum flow-rate for hydrogen exists at 25 ml/min. Less than optimum, a measurable decrease in the peak area is obtained.

Since MOCA appears on the tailing edge of the acetone peak, the effect of the solvent volume on the peak area of MOCA was also investigated. A constant amount of MOCA was introduced into the gas chromatograph with varying amounts of acetone. The peak area of MOCA as a function of the solvent volume is shown in Fig. 2.

The solvent effect is pronounced. With increasing volume of acetone to introduce a constant amount of MOCA, a rapid decrease in the sensitivity of the



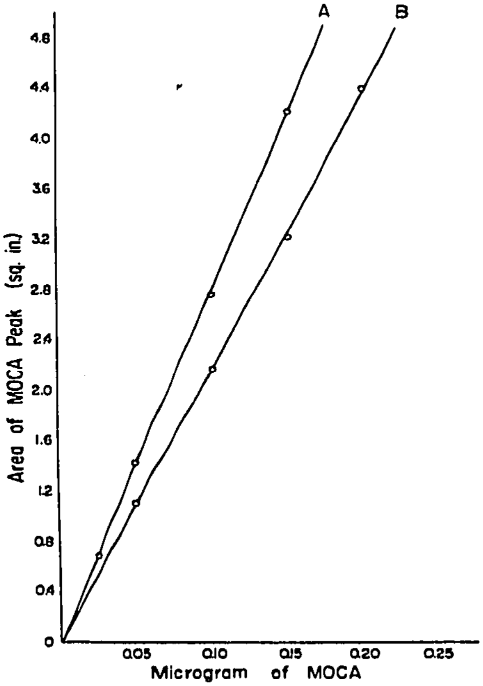


Fig. 2. Effect of the solvent volume on the peak area of MOCA. A = 0.025 μg MOCA; B = 0.050 μg MOCA; C = 0.100 μg MOCA; D = 0.150 μg MOCA; E = 0.200 μg MOCA.

Fig. 3. Calibration curves of MOCA. A = 1-μl aliquot; B = 2-μl aliquot.

method is noted. This effect can be controlled by using a constant volume of solvent. Calibration curves prepared with 1- and 2-μl aliquot samples were linear with slopes of 28 and 21.8 sq. in./μg of MOCA (see Fig. 3).

In selecting a solid sorbent for sampling MOCA in air, a different set of analytical parameters was taken into consideration. A small, inert, and efficient sorbent tube that can be readily assembled and disassembled for extraction were some of the essential features for the collector. To evaluate these features, solid sorbents were screened by static testing. Known amounts of sorbent were placed in 1-ml volumetric flasks, and 5 and 10 μg of MOCA dissolved in acetone were applied directly on the sorbent. These samples were stoppered and allowed to equilibrate at ambient temperature for 24 h. Extraction was accomplished by adding 0.5 ml of acetone and allowing the samples to stand for 25–30 min with occasional stirring. A 2-μl sample was then analyzed by the GC procedure. Of the sixteen sorbents tested, only Gas-Chrom S proved to be promising. Further testing showed that this sorbent had an average desorption efficiency of 92% toward MOCA (see Table I).

Of equal importance is the collection efficiency of Gas-Chrom S toward MOCA in air. This property was evaluated by dynamic testing. In this case, the sorbent was packed as two separate sections, 10 and 50 mg, with small amounts of quartz wool plugs into a 2½-in. × ¼-in.O.D. Pyrex tubing that was tapered on one end (see Fig. 4). A known concentration of MOCA in air was generated by placing

TABLE I

RECOVERY OF MOCA FROM GAS-CHROM S SORBENT BY STATIC TESTING

No. of determinations	*Amount of MOCA*		*% Recovery*	*Relative standard deviation (%)*
	Applied (μg)	*Found (μg)*		
5	5.0	4.60	91	1.7
5	10.1	9.30	92	0.0
5	20.2	19.03	94	0.7

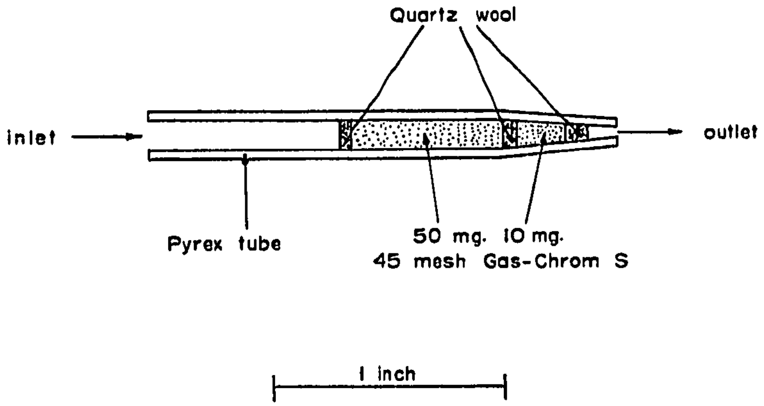


Fig. 4. MOCA sampling tube.

TABLE II

COLLECTION DATA OF MOCA IN AIR ON A GAS-CHROM S TUBE

Oven temperature (°C)	*No. of determinations*	*Sampling rate (l/min)*	*Length of sampling (h)*	*MOCA found in sorbent (μg)*		*Concentration of MOCA in air* (μg/l)*
				First section	*Second section*	
23	1	1	1	0	0	0
23	1	1	2	0	0	0
23	1	1	3	0	0	0
23	1	1	6	0	0	0
23	5	1	8	0	0	0
120	3	1	0.5	1.89	0	0.063
120	1	1	1	3.90	0	0.065
120	5	1	8	32.60	0	0.068

* 25° and 585 mmHg at Los Alamos, N.M., U.S.A.

MOCA in a diffusion chamber located in a temperature-controlled oven, and by purging the chamber with air at a rate of 1 l/min. Immediately at the outlet of the chamber, a Gas-Chrom S tube was fastened with PTFE Swagelok fittings such that the initial absorption of MOCA occurred on the 50-mg section.

The inlet of the absorption tube was essentially at the oven temperature, and the remaining portion was at ambient temperature. After a specified length of sampling, each section of Gas-Chrom S with its wool plug was transferred from the tube into a 1-ml volumetric flask and extracted separately with 0.5 ml of acetone for analysis. The results from this study are summarized in Table II.

The collection efficiency of Gas-Chrom S in this tubular configuration is 100% for MOCA in air. It is also obvious that the first section retains all the MOCA up to 8 h of sampling at 1 l/min. Hence, the collector is acceptable as a personal sampler. The selection of 120° for generating MOCA in air is practical, since the preparation of castable Adiprene polymer at this laboratory involves preheating of MOCA slightly above its melting point prior to reacting with heated Adiprene prepolymer.

Procedure

MOCA in air is sampled at a rate of 1 l/min (up to 8 h) through a Gas-Chrom S tube with the aid of a Bendix personal air sampling pump or its equivalent. The tapered end of the tube is attached to the pump so that the initial air sampling occurs on the 50-mg section. After sampling, each section of the Gas-Chrom S with its plug is transferred into a 1-ml volumetric flask and 0.5 ml of acetone is added to extract the collected MOCA. The sample is allowed to stand for 25 min with occasional stirring and an aliquot sample is analyzed gas chromatographically.

A flame ionization gas chromatograph, equipped with a silylated glass liner and a 1-ft. 10% Dexsil 300 GC column, is operated at column and inlet temperatures of 200 and 265°, respectively. The flow-rate of the helium carrier gas is adjusted to 35 ml/min, and the flow-rate ratio of helium to hydrogen to air is maintained at 1:0.71:10. After the recorder has been turned on, the electrometer is balanced and the FID is ignited. The electrometer range switch is set at 100 and the attenuation is lowered to ×4. Two microliters of the acetone extract are injected into the gas chromatograph with the Hamilton microsyringe held in the sample inlet until the acetone peak, as displayed on the recorder, goes off-scale and then returns on-scale. At this point, the syringe is withdrawn. After 2–3 min, the range switch is reset to 0.1 and a complete chromatogram is obtained in 13 min. The peak area of MOCA is measured by the peak height multiplied by peak width at half-height method and the concentration is determined from a calibration curve prepared with a 2-μl aliquot of standard solutions. At low MOCA concentration an increase in the sensitivity is achieved with a 1-μl sample provided the calibration curve is also prepared with the same volume of the standards. MOCA in milligrams per cubic meter of air is then calculated by the following relationship:

$$\text{mg MOCA/m}^3\text{ of air} = \frac{\mu\text{g MOCA found} \times A \times 1.087}{\text{Sampling rate (l/min)} \times \text{length of sampling (min)}}$$

where $A = 250$ for a 2-μl aliquot sample and 500 for a 1-μl aliquot sample.

RESULTS AND DISCUSSION

The precision and accuracy of the method were established by analyzing synthetic mixtures of MOCA at several concentrations. The results are shown in

TABLE III

ANALYSIS OF SYNTHETIC MOCA SAMPLES

No. of determinations	*Amount of MOCA*		*Relative standard deviation (%)*
	Analyzed (µg)	*Found (µg)*	
5	0.020	0.019	5
5	0.050	0.050	2
5	0.100	0.100	2
5	0.150	0.149	1.3

Table III. Within the concentration range of 0–0.150 µg of MOCA, excellent results were obtained, with relative standard deviations of less than 5%. Typical chromatograms are shown in Fig. 5. A small amount of an unknown product appears after MOCA, but it does not interfere with the analysis.

Air and swipe samples were obtained from a MOCA processing facility and these samples were also analyzed by this procedure. With all ten air samples collected from controlled MOCA operations on Gas-Chrom S tubes, the extracts contained no MOCA. The chromatograms were identical to that of the acetone solvent. The absence of MOCA in the air samples substantiates our earlier findings (see Table II) that no MOCA in air was generated at 23°. The contributing factors are the low

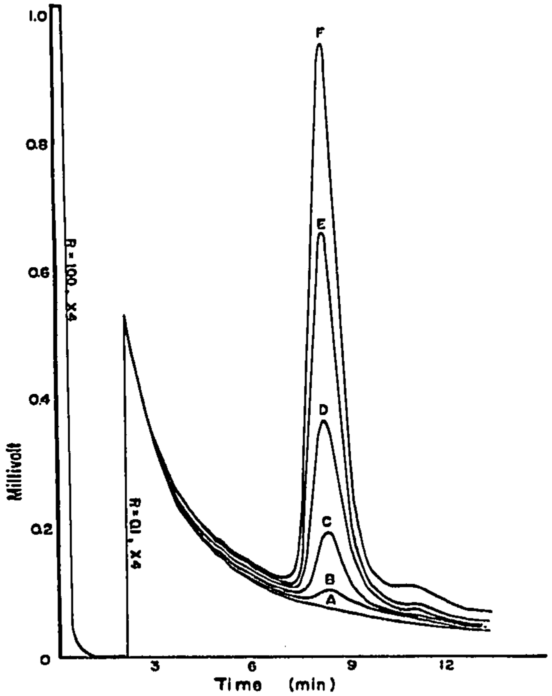


Fig. 5. Chromatograms of MOCA. Constant volume = 2 µl. A = Acetone; B = 0.005 µg MOCA; C = 0.020 µg MOCA; D = 0.050 µg MOCA; E = 0.100 µg MOCA; F = 0.150 µg MOCA.

vapor pressure of MOCA, estimated to be 5×10^{-6} mm at 20°, and the severe controls imposed by federal regulations.

Similar results were obtained from the swipe samples; however, eight out of the ten samples showed one to five impurities. Fortuitously, none of the impurities had the same retention time as MOCA to cause an interference. To verify our results, a spiked sample was prepared with the extract from one of the swipe samples such that the 2-μl sample used for analysis contained 0.010 μg of MOCA. The chromatogram clearly shows MOCA.

To avoid excessive laboratory analysis, a convenient chemical test was also developed for field testing of MOCA in a contaminated area. Although the test is nonspecific, it provides a rapid means to assess the extent of contamination. The colorimetric test is based on the Ehrlich reaction, in which the primary aromatic amine, such as MOCA, condenses with *p*-diethylaminobenzaldehyde (*p*-DEAB) to produce a bright, yellow dye. To perform this spot test, a swipe sample is obtained on a Whatman filter paper and a drop or two of 0.25% *p*-DEAB dissolved in 0.25 *N* ethanolic HCl is applied on the paper. The appearance of a yellow color indicates the presence of a primary aromatic amine. In that event, additional samples can be obtained for laboratory evaluation. With MOCA, a 0.5-μg sample is sufficient to produce a positive test on the filter paper.

In selecting Gas-Chrom S for MOCA, it was observed that the extracts from several solid sorbents produced unusual chromatograms. For example, activated silica gel and alumina apparently react with MOCA to produce two additional products on the chromatogram. Although the identity of these products is not known, a possible explanation is the abstraction of HCl from MOCA by the active sites of the sorbents. With an increase in the activation of the sorbent, the concentration of the by-products increases proportionately with a corresponding decrease in the MOCA concentration.

The detection limit of this method was briefly investigated. With a 1-μl aliquot sample, 0.002 μg of MOCA can be readily detected. This is a factor of two better than the Stouder's procedure using the ECD.

Interference can be expected from any organic compounds having an identical retention time as MOCA. However, isomers of chloroanilines commonly associated with MOCA do not interfere as they are completely resolved from MOCA.

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