

Enhancement of Electron-Capture Detection of Chlorocarbons by Iodination

Andrew J. Watson*

Space Physics Research Laboratory, University of Michigan, Ann Arbor, Michigan 48109

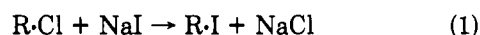
Gwendolyn L. Ball

Department of Environmental and Industrial Health, University of Michigan, Ann Arbor, Michigan 48109

Donald H. Stedman

Department of Atmospheric and Oceanic Science, University of Michigan, Ann Arbor, Michigan 48109

The selective electron capture sensitization (SECS) techniques described so far in the literature involve doping the carrier with traces of a second gas, in particular oxygen (1-3) and N_2O (4). Here we report a SECS technique of a different sort: the sample is passed over a reagent just prior to the detection stage of analysis. The compound of interest reacts selectively to evolve a product with a high electron affinity, to which the electron-capture detector (ECD) is sensitive. In our experiments the reagent was sodium iodide, and the compounds to be determined were certain chlorocarbons normally poorly detected by the ECD. The reaction used for detection was the substitution of an iodine atom for chlorine.



The response of the ECD toward halocarbons is generally greatest for iodides and decreases through the bromine, chlorine, and fluorine derivatives. Provided, therefore, that the yield of reaction 1 is large enough, very significant enhancement of signal may be achieved by detecting the iodide rather than the chloride. In this work we have concentrated on the determination of methyl chloride in air; we find a sensitization by a factor greater than 10^4 over the direct analysis.

EXPERIMENTAL SECTION

Apparatus. The electron-capture gas chromatograph was a Shimadzu GC-R1A equipped with a ^{63}Ni detector of the pulse frequency feedback type. The column used for separations was 2 m \times 6.4 mm o.d. stainless steel packed with Porasil B 80-100 mesh. The carrier gas was oxygen-free nitrogen at a flow rate of 30-40 mL/min. Gas samples were introduced via a sampling valve equipped with a 5.0-mL loop. The gas chromatograph-mass spectrometer was an AEI MS 30 double-beam instrument coupled to a Pye Series 104 chromatograph via a silicone membrane separator.

Procedure. Sodium iodide (minimum purity 99%) was ground, sieved (40-100 mesh), and packed into a 1 m \times 3.2 mm o.d. stainless steel tube. NaI is deliquescent, and it was necessary to carry out the preparation of the reaction tube as rapidly as possible to avoid excess uptake of moisture, which otherwise caused the tube to block. Mixing 25% by volume "Chromasorb W" stationary phase support with the sodium iodide helped to alleviate this problem. Immediately after being packed the reaction tube was heated to 410 °C and connected to a flow of argon-5% methane gas. The tube was maintained at this temperature for several days to allow it to dry and condition.

The setup for analysis by gas chromatography is shown in Figure 1. Since the reaction tube was operated at a higher temperature than the detector, a short length of column packing was added between the two to ensure that no compounds eluting from the reaction tube would condense in the detector. A valve was provided by which the effluent from the analytical column could be vented to the atmosphere and was used to switch out the oxygen peak during analysis of air. This was found to be desirable because exposure of the reaction tube to oxygen promoted formation of an unknown compound (probably iodine vapor) which would then "bleed" into the carrier gas, interfering with the analysis and causing an unsteady base line.

Table I. Iodination of Chlorocarbons by NaI at 350 °C

compound	product(s)	approx effi- ciency, %
methyl chloride	methyl iodide	80
ethyl chloride	ethyl iodide	80
benzyl chloride	benzyl iodide	50
dichloromethane	diiodomethane	50
	iodine	
	chloroiodomethane	
vinyl chloride		0
chlorobenzene		0

For analysis by GC-MS, the setup was identical with Figure 1, but the ECD was disconnected and the eluent was instead collected for subsequent analysis.

Calibration. The methyl chloride determinations were calibrated against standard dilutions of 800 pptr (parts per trillion) methyl chloride in nitrogen, stored at a pressure of 30-50 psig in stainless steel cylinders. The standards were prepared by a single static dilution of calibration gas, supplied by Matheson (5 ppm of CH_3Cl in air), into nitrogen.

RESULTS AND DISCUSSION

Optimization. Some "fine tuning" was required to obtain a good signal with a minimum of bleed from the reaction tube. The bleed could be cured by adding 2% hydrogen to the nitrogen carrier gas, while at the same time heating the sodium iodide to 410 °C for several hours. This suggests that bleed was reduced to a minimum when all traces of oxidant were removed from the system. However, passing H_2 through the apparatus also greatly attenuated the response to methyl chloride, an observation which is consistent with that of Miller and Grimsrud (5). The attenuation is probably due to the reaction of CH_3I with the H_2 -activated surfaces of the system. The response could be progressively restored with the minimum of bleed by allowing a few samples of whole air—including the oxygen peak—to traverse the system. Once optimum conditions were established they could be maintained almost indefinitely provided that subsequent air peaks were not allowed to enter the reaction tube.

Compounds Which Undergo Iodination. By use of the mass spectrometer, a number of compounds were tested for participation in reaction 1, as shown in Table I. When the chlorine is adjacent to a double bond, the compound is unreactive up to reaction tube temperatures of 420 °C, possibly arising from the increased C-Cl bond strength. However, one or two chlorine atoms bonded to a saturated carbon atom are readily displaced by iodine. Since singly chlorinated compounds are normally the most difficult to detect with the ECD, the method may give useful signal enhancement for a number of substances besides methyl chloride.

Temperature Dependence of the Response. In Figure 2 we have plotted the signal due to methyl chloride as a function of temperature of the reaction tube. The increase

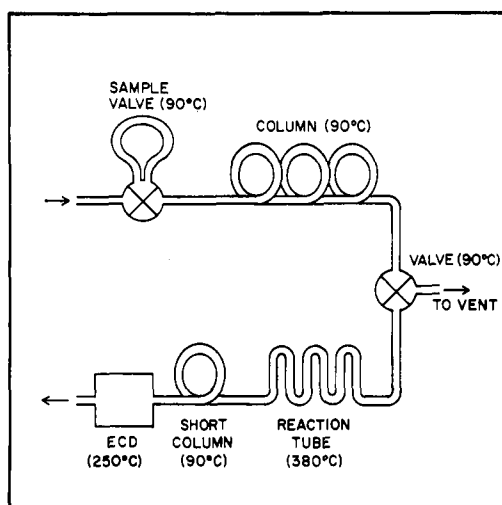


Figure 1. Schematic diagram of apparatus used for analysis by gas chromatography with iodination. The temperatures at which the components were maintained are shown in brackets.

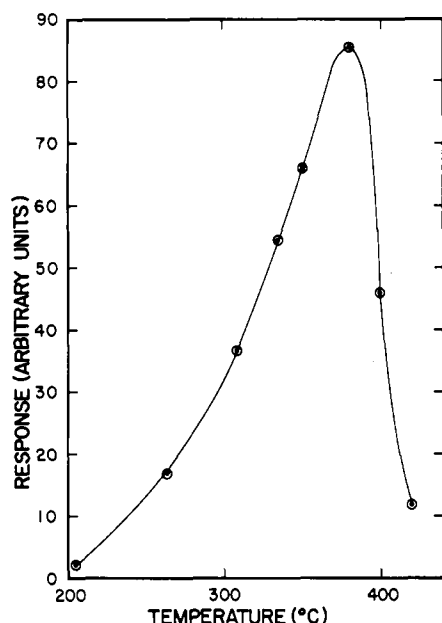


Figure 2. The response of the ECD to methyl chloride (arbitrary units) with temperature of the reaction tube. Each point on the graph is the average of four or more determinations. The standard deviations are of the same order or smaller than the size of the points.

in response with temperature below 380 °C is consistent with the yield of methyl iodide from reaction 1, as measured by the mass spectrometer. By calibrating the GC-ECD for methyl iodide response, we were able to confirm that, at the optimum temperature of 380 °C, at least 90% of the CH_3Cl in the sample was converted to CH_3I . The sharp falloff in the observed response above 380 °C is probably due to thermal decomposition of methyl chloride or methyl iodide. Because the temperature dependence is rather sharp, a stable reaction tube temperature was essential to maintain good precision. A change in temperature of 2 °C could result in a fluctuation of 5% in the response.

In our experiments good thermal stability at an accurately known temperature was achieved by placing the reaction tube in a separate oven, the oven temperature being monitored by thermocouples. A more convenient arrangement which also appears to give adequate stability consists of mounting the reaction tube in a separately heated, insulated aluminum block. The block is placed within the GC oven and heated via a proportional temperature controller.

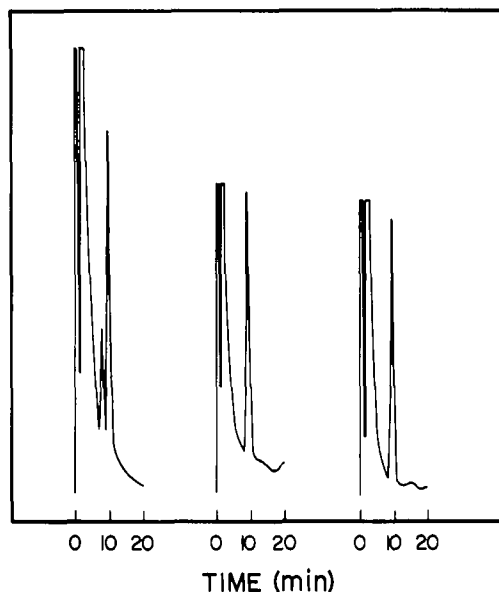


Figure 3. At left, analysis of outside air containing 950 pptr CH_3Cl (large peak at approximately 10 min). The smaller peak just preceding CH_3Cl is CCl_3F . Center and right, repeat analyses of 800 pptr CH_3Cl in nitrogen.

When the temperature was stabilized, the precision of the method was better than 2% when making a series of determinations of an 860 pptr standard over a period of 3 h. The minimum detectable level was 31 fg, corresponding to 3 pptr of methyl chloride in a 5-mL sample of gas at room temperature. With the reaction tube removed from the GC system, the sensitivity to methyl chloride was a factor of more than 10^4 less. We note, however, that our system was not optimized for this measurement; detection limits of approximately 4 pg have been reported by Singh et al. (6), apparently without the use of any technique of sensitization.

Application to Atmospheric Determinations of CH_3Cl

Figure 3 shows a chromatograph of outside air obtained by this technique together with two calibrations of 800 pptr CH_3Cl in nitrogen. The air was sampled near Ann Arbor, MI, and contains an unusually high concentration (950 pptr) of CH_3Cl . The mean concentration in air near Ann Arbor has been measured to be 630 pptr (7), but high levels such as this sample are occasionally observed and may reflect a local urban source.

As Grimsrud and Miller (1) and Rasmussen (3) have shown, ECD response to methyl chloride is also enhanced by the oxygen doping technique of SECS. However, the iodination technique reported here provides greater sensitization; previously the best reported direct determinations of atmospheric methyl chloride quoted a sensitivity of 60 pptr and precision of 4% at the 800-pptr level (3). High sensitivity can be obtained by cryogenic preconcentration of air samples (3, 8, 9); cryotrapping is a relatively laborious and imprecise method, however, and direct analysis is preferable if it is feasible.

We anticipate that the application of this method to determinations of atmospheric and oceanic methyl chloride will help to extend the data base on the environmental distribution of this gas. Because of the difficulty of the analysis, relatively few investigations of atmospheric CH_3Cl have been reported by comparison with the other important halocarbons in the atmosphere. Although it is the most abundant halocarbon, the presence of CH_3Cl in air was not even discovered until 1975 (10, 11), several years after CCl_3F , CCl_2F_2 , and CCl_4 had been measured (12). The development of a sensitive and accurate measurement technique may help to answer a number of questions concerning the sources of CH_3Cl (7), its residence time in the atmosphere, and possible future increases

in concentration (due to either anthropogenic perturbations of atmospheric chemistry (13) or direct emissions).

ACKNOWLEDGMENT

The authors wish to thank J. E. Lovelock and R. A. Rasmussen for helpful discussion on this subject and the National Science Foundation Atmospheric Science Section for support.

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RECEIVED for review August 29, 1980. Accepted October 22, 1980.

Electrode Positioner for Laser-Enhanced Ionization Spectrometry

George J. Havrilla¹ and Robert B. Green*

Department of Chemistry, Chemistry Building, University of Arkansas, Fayetteville, Arkansas 72701

Recent studies (1, 2) have demonstrated that an electrode positioner is necessary for optimization of the laser-enhanced ionization (LEI) signal. In LEI spectrometry, a dye laser tuned to a discrete absorption transition of an analyte atomized in a flame enhances the thermal (collisional) ionization of the analyte atoms. The laser-related increase in ionization is detected with electrodes held at a negative high voltage and measured with conventional electronics. The laser beam is directed between the electrodes and parallel to the slot of a premix burner. An electrode positioner is necessary to determine the position of the electrodes with respect to the burner head and laser beam once that relationship is fixed.

The rest of this paper will describe the important features of an electrode positioner designed for LEI spectrometry and illustrate them with experimental data. The electrode positioner (see Figure 1) incorporates the necessary versatility for optimizing signals and the mechanical stability for precise positioning in a simple design. The primary functions of the positioner are the vertical translation and horizontal separation of the electrodes.

Vertical translation of the electrode holder assembly (B) is accomplished by revolving a knurled wheel (A-4) which turns a $1/4$ in. \times 20 in. threaded steel rod (A-1) in the translation base (A-8). Twenty threads per inch provides about 1 mm travel of the vertical translation column (A-3) per revolution of A-1. Horizontal stability for the electrodes is maintained by the two $3/8$ in. diameter brass rods (A-2) which track parallel to the threaded rod (A-1). This prevents yawing of the electrodes and maintains them in a level, parallel position during vertical translation.

The unique feature of the positioner is the electrode holder assembly (B). The basic element is the dual-threaded hori-

Table I. Effect of Plate Separation on the LEI Signal

separation (mm)	LEI signal (arbitrary units)
11.5	38
12.0	10
12.5	1

Table II. Effect of Rod Separation on Matrix Concentration Range

separation (mm)	% LEI signal recovery						
	2 $\mu\text{g}/\text{mL}$ Na	5 $\mu\text{g}/\text{mL}$ Na	10 $\mu\text{g}/\text{mL}$ Na	15 $\mu\text{g}/\text{mL}$ Na	20 $\mu\text{g}/\text{mL}$ Na	30 $\mu\text{g}/\text{mL}$ Na	40 $\mu\text{g}/\text{mL}$ Na
9	158	161	158	147	139	47	1
10	159	152	134	63	1		
11	144	127	8				
12	133	25					

zontal translation rod (B-1). B-1 is a $3/8$ in. diameter brass rod with both right- and left-hand threads (24 threads/in.) originating at the center. This causes the threaded electrode holder mounts (B-2) to move in opposite directions along B1 when the adjustment knob (B-5) is turned; i.e., both electrodes move toward the center or toward the ends when B-5 is turned counterclockwise or clockwise. The electrode holder mounts maintain a fixed orientation as they move along B-1 because they slide along a track (B-6). The synchronous movement of the electrode holders maintains the flame in a centered position between the electrodes without additional adjustments. One revolution of B-1 results in 1 mm horizontal travel for each holder, i.e., 2 mm separation or closure of the electrodes per revolution. A finer thread would, of course, yield greater resolution in electrode separation. A more advanced

¹ Present address: Center for Analytical Chemistry, Rm. 212, Bldg. 222; U.S. National Bureau of Standards; Washington, DC 20234.