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Qualitative Detection Limits for Specific Compounds Utilizing Gas Chromatographic Fractions, Activated Charcoal and a Mass Spectrometer

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Qualitative identification of gas chromatograph (G.C.) fractions has created problems for the organic chemist. One of these concerns the limit of detection for any given compound which can be achieved with a method designed to trap a G.C. peak for further analysis. This paper presents the limits of detection found attainable in the qualitative analysis of specific organic compounds. These limits were established by utilizing an activated charcoal capillary to trap the G.C. fraction prior to introduction into a Bendix Time-of-Flight mass spectrometer via the hot filament probe.

Introduction

LABORATORY PERSONNEL of the Bureau of Occupational Safety and Health are often called on to sample and to analyze for industrial solvents in the ambient air from the occupational environment. Activated charcoal tubes are used to collect an integrated sample and to concentrate the solvent vapors. These solvents are desorbed with a suitable agent and are separated by employing gas chromatographic (G.C.) procedures.[1]

Qualitative identification of G.C. peaks has created many problems for the industrial hygiene chemist. He is often concerned with the limit of detection for any given compound when a gas chromatograph–mass spectrometer (G.C.–M.S.) system is utilized. With a G.C.–M.S. interface system, the chromatograph fraction is diluted by the carrier gas, thereby adversely affecting the sensitivity limit.[2-5] Trapping of individual fractions by the freeze trap method would enable the analyst to concentrate the sample for increased sensitivity, but this is very time-consuming and may involve unwanted condensation.[6-7]

In 1965, Amy *et al.*[8] proposed utilizing a melting point capillary packed with about 5 mg of conditioned column packing to collect the sample. Damico *et al.*[9] used a small capillary tube packed with 20 mg of activated charcoal as the collection-concentration medium. The capacity of the activated charcoal for retaining the organic compound of interest is much greater than that of the column packing.[8,9] Also, organic compounds are stable on activated carbon and can be analyzed after long periods of time in storage.[1,9]

Almost all organic vapors are normally found in mixtures in the industrial atmosphere, thereby requiring an analysis capable of simultaneously separating and qualitatively identifying the components. Although retention time is widely used in gas chromatography to make qualitative identifications, the possibility always exists of other compounds having the same retention time. An occupational health laboratory must analyze samples from foundries, factories, laboratories, and other work sites which contain organic compounds of unknown identity. A

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means was sought whereby these unknown peaks could be analyzed with a mass spectrometer in order to determine their identity.

This paper presents the limits of detection used in the qualitative analysis of specific organic compounds. These limits were established by utilizing a capillary tube containing activated charcoal to trap the G.C. fraction prior to introduction into the Bendix Time-of-Flight mass spectrometer via the hot filament probe.

Experimental Procedure

Experimental Apparatus and Reagents

Perkin-Elmer Model 900 gas chromatograph equipped with dual flame ionization detectors and a 10:1 splitter assembly.

Variac connected to a heating coil around a 1/16-inch swage fitting which is fastened to the splitter outlet.

Bendix Time-of-Flight mass spectrometer equipped with a Model 843A direct inlet probe.

Spectrograde and reagent-quality solvents.

Activated charcoal, 20/40 mesh.

Glass capillary tubes, 25 mm × 1 mm I.D.

Associated laboratory hardware and supplies.

Collection and Concentration of Samples

Activated charcoal tubes were used to take integrated industrial atmospheric air samples. Glass tubes (4 mm I.D.) were packed with two 1-inch sections (180 mg each) of 20/40-mesh activated charcoal, which were separated and retained with plugs of fiberglass. The flame-sealed ends were broken in the field and the ambient air sample was taken, a portable pump being used to draw a measured amount of air through the charcoal tube. They were then resealed and transferred to the occupational health laboratory for analysis.[1]

Preparation of Gas Chromatograph Standard Curves

Optimum G.C. operating parameters and column conditions were determined experimentally for the complete and rapid separation of specific solvents from mixtures.[1] Then standard curves were prepared for the quantitative estimation of each such solvent. Known quantities of solvent, carefully measured and calculated to be within the desired range of concentrations (ppm) on the basis of 10-liter air samples at 25°C, were introduced into the G.C. to obtain the standard series of peak heights (and areas). These standards were used in determining the lower limits of detection and determination.

Trapping of Gas Chromatograph Fraction

A 10:1 splitter assembly was installed within the manifold of the G.C. A Variac was connected with a heating coil which was wrapped around the splitter outlet to minimize vapor condensation before the sample reached the collector charcoal tube. Inasmuch as the sample had originally been trapped on activated charcoal, a 25-mm × 1-mm glass capillary collector tube was fashioned with a plug of glass wool at one end to retain about 4 mg of activated charcoal. This capillary collector tube was then inserted into a 1/16-inch swage fitting and tightened to assure total adsorption of the emerging fraction on the activated charcoal. The tube is inserted as the peak of interest starts appearing on the strip chart chromatogram and is withdrawn as the peak returns to the base line.

Mass Spectrometric Analysis

After collecting the fraction of interest, the tube was placed on top of the thermocouple in the heating element of a Bendix Model 843A direct inlet probe. Care was taken to ensure that none of the charcoal was lost in the process, since most of the sample was collected on the charcoal near the top of the tube.

The direct inlet probe was then inserted through a vacuum lock into the ion chamber of the Time-of-Flight mass spectrometer. Since qualitative limits of detection using the capillary tube were of interest, sensitivity was greatly enhanced by exposing the entire sample to electron bombardment. The probe temperature was increased gradually so that the sample could be released from the activated charcoal for recording of the mass spectrum.

Discussion of Results

The limits of detection for 26 compounds

Table I
Limits of Detection

Compound	Parts per million	Micrograms
Isoamyl acetate	10	2.4
Benzene	20	2.9
2-Butanone	20	2.6
n-Butyl acetate	20	4.2
Isobutyraldehyde	10	1.5
n-Butyraldehyde	25	3.3
Carbon tetrachloride	20	5.6
Chloroform	20	4.4
Crotonaldehyde	10	1.3
1,2-Dichloroethane	10	1.8
p-Dioxane	20	3.2
Ethanol	50	4.2
Ethyl acetate	25	4.0
Ethylbenzene	10	1.9
Ethyl ether	10	1.3
Heptaldehyde	25	5.2
Heptane	10	1.8
Hexane	20	3.1
Methylene chloride	20	3.1
Perchloroethylene	20	6.1
Propionaldehyde	25	2.7
Isopropyl alcohol	20	2.2
Toluene	25	4.2
Trichloroethylene	20	4.9
Isovaleraldehyde	10	1.6
n-Valeraldehyde	25	3.9

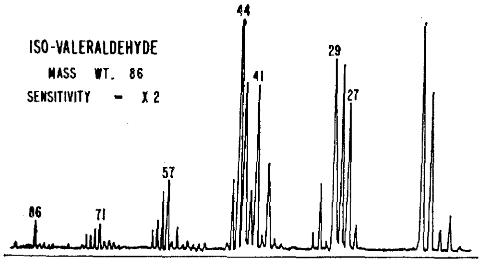

FIGURE 1. Mass spectrum of isovaleraldehyde at 10 ppm.

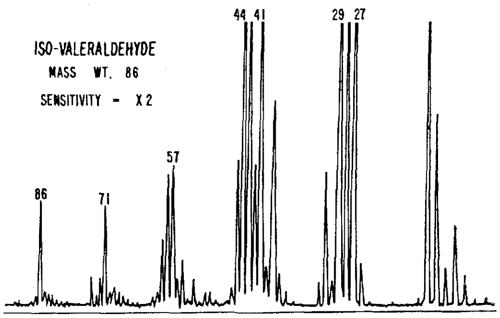

FIGURE 2. Mass spectrum of isovaleraldehyde after replica trappings.

of occupational health significance are displayed in Table I. The values shown in the parts-per-million column were determined experimentally and represent a sample volume of 10 liters of ambient air. These limits were obtained by analyzing samples of known concentrations by the G.C.–M.S. procedures described above. The microgram column represents the amount of compound which must be trapped by the capillary charcoal tube during a single trapping of a G.C. peak in order for a positive identification to be made with the mass spectrometer.

If the compound is present in an amount below its respective limit of detection, then replica trappings of the peak can be made to make more probable a positive identification. Figures 1 and 2 compare the mass spectrum of isovaleraldehyde at its detection limit of 10 ppm with its mass spectrum after several trappings were made of the G.C. peak to concentrate the sample. Background peaks from the desorbant ethyl ether and the CO and CO_2 from charcoal begin to interfere, so that identification of isovaleraldehyde becomes increasingly difficult at values below the listed detection limit.

Summary

This paper describes a complete method suitable for quantitatively measuring and qualitatively identifying atmospheric organic vapors. A charcoal tube was employed as the sample collection-concentration medium; a G.C. was employed to separate and quantitate the organic mixture, and a charcoal capillary tube was employed to trap and transfer the G.C. peak to the mass spectrometer for qualitative identification.

This paper also presents the limits of detection determined in the qualitative analysis of 26 specific organic compounds. These limits were established by utilizing an activated charcoal capillary tube to trap the G.C. fraction prior to introduction into a Time-of-Flight mass spectrometer via the hot filament probe.

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Thermal Analysis

The National Bureau of Standards has released a report on the *Proceedings of a Symposium on the Current Status of Thermal Analysis* held at Gaithersburg, Maryland, April 21-22, 1970. Nine symposium papers in this report focus attention on recent trends and needs in the field of thermal analysis. The contents can be classified under the following topics: (a) discussions of the importance of experimental parameters for obtaining information from differential thermal analysis, (b) evaluation of errors of classical calorimetric measurements, (c) review of progress in developing standards for temperature calibration based on dynamic measurements, (d) providing a representative sample of thermal analysis applications in high temperature measurements and in studies of biochemical, polymer, and explosive materials, (e) evaluation of errors in differential scanning calorimetry, and (f) modifications of thermogravimetric apparatus for kinetic studies.

Copies of this report may be obtained for $1.00 per copy from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 20402. In ordering please specify National Bureau of Standards Special Publication 338.

Fatalities in Coal Mines

The U. S. Bureau of Mines reports that the work fatalities in the coal mining industry totaled 255 in 1970 and occurred at frequency rates of 1.01 per million man-hours of work time and 0.43 per million tons mined. The 1970 record was sharply worse than in 1969 when the total number in frequency rates of fatalities were lowest in a statistical history started in 1930. In 1969, 203 men lost their lives in coal mines and the frequency rates were 0.85 and 0.36 respectively. The retrogression in the over-all record for 1970 resulted entirely from the worsened experience at bituminous coal and lignite mines which more than off-set the appreciably better record at anthracite mines. One major disaster in 1970 took 39 lives whereas there were no major disasters in 1969. The record relative to fatalities from falls of roofs, face and rib was slightly improved in 1970 whereas the record for fatalities from gas explosions was sharply worsened. There continues to be an upward trend in the frequency rate of fatal injuries from machinery accidents whereas the frequency for underground haulage accidents continues at the same level.