SURVEY AND DETERMINATION OF TRACE COMPONENTS IN AIR BY SERIAL MASS-FRAGMENTOGRAPHIC RUNS OVER THE ENTIRE MASS RANGE

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SUMMARY

A new, sensitive and precise gas chromatographic–mass spectrometric method is described for the survey and the determination of trace components in air. The method involves serial mass-fragmentographic runs over the entire mass range studied (which we have termed survey mass fragmentography), with direct injection of 50 ml of the air sample on to a cryogenic gas chromatograph combined with a quadrupole mass spectrometer; no concentration, extraction or collection of the compounds on adsorbents is required.

INTRODUCTION

The determination of mixtures of trace compounds in air is a fundamental analytical problem in studies of atmospheric pollution. As the concentration of each component is generally very low, the primary requirement for the analysis is that the detection system should have high sensitivity and adequate reliability.

Gas chromatography–mass spectrometry (GC–MS) is one of the most useful techniques that satisfies these requirements. However, when the concentrations of the individual components in the air are low, the usual GC–MS method requires a prior concentration step. The concentration procedures commonly used are solvent extraction[1], condensation in a cold trap[2] or collection on adsorbents[3], such as charcoal or Tenax GC[4].

Each of these techniques has several associated difficulties. To achieve adequate sensitivity when a solvent-extraction procedure is used, the solvent must be reduced in volume (usually by evaporation), and this process may cause significant loss of volatile components and a concentration of contaminants in the solvent. The cold-trap method, on the other hand, which is used for the pre-concentration of volatile organic compounds from air, generally collects a significant amount of condensed water, which interferes with the subsequent analysis. Generally, in ambient air, water vapour is one of the major components, and, at 25° and 50% relative humidity, 1 l of air contains over 11 mg of water vapour. This procedure, therefore,

requires further processing to isolate the organic compounds from water after the cold-trap condensation of several litres of air.

Charcoal or porous polymer adsorbents can also be used quantitatively to collect organic compounds from air. However, recovery of the components from the adsorbent is usually incomplete and variable. It is thought that such adsorbents may serve as catalysts for reactions between the adsorbed substances.

To overcome the above-mentioned difficulties, the direct injection of very small volumes of air on to a cryogenic gas chromatograph combined with a mass spectrometer was investigated. Since no pre-treatment is necessary before the injection, this is the simplest of all methods, offering significant advantages. The detection limits are, however, inadequate for practical purposes, as the method involves no concentration step. Selective ion monitoring[5] (mass fragmentography) is an appropriate approach to meet the sensitivity requirements and to compensate for the incompleteness of the gas-chromatographic separation. In conventional mass frag-mentography, the species monitored are those yielding the base peaks and the molecular ions of the substances to be determined. When the composition of the sample is unknown and the identification of the components is required, specific m/e values cannot be chosen and the mass fragmentograms should be examined for all m/e values.

A new GC–MS method for the determination of trace components in air samples is described in this paper. This method is based on mass fragmentography over the entire mass range (from m/e 11 to 100 in the present study) and direct injection of a small volume of air into the cryogenic GC–MS system. This method we have tentatively terme. survey mass fragmentography (SMF), and it has been applied to the survey of trace compounds in air from the Tokyo region.

SURVEY MASS FRAGMENTOGRAPHY

SMF is defined as serial mass-fragmentographic runs over the entire mass range studied. A mass spectrum can be reconstructed by compiling those peaks that have identical retention times on the survey mass fragmentograms. The technique has the following advantages: (1) the sensitivity, specificity, and yield of quantitative in-formation are similar to those of conventional mass fragmentography; (2) the mass spectra can be readily interpreted; and (3) it provides for the survey and detection of all the trace components at a sensitive level.

In comparison with that of mass chromatography[6], the detection limit by SMF is better by 2 or 3 orders of magnitude. When SMF is applied to air analysis, trace organic compounds can be determined by direct injection of a small sample and without interference from water vapour. Although this method is in itself time-consuming, there is compensation for this drawback, as no extraction, concentration or collection on adsorbents is required.

EXPERIMENTAL

Instruments

A Hewlett-Packard 5992A gas chromatograph–mass spectrometer–calculator system was used. The mass spectrometer was equipped with an electron-impact ion

source, and the calculator provided computerization of the gas chromatograph–
mass spectrometer, making operation of the instrument very simple. The program
cassette tape was inserted to begin the autotune operation of the mass spectrometer
and to achieve the keyboard commands. After the autotune operation was auto-
matically completed, a report of the calibration result was given. Then the software
needed to make a mass-fragmentographic run was called from the tape, after which
choices had to be made for selection of up to six ions. The resulting selected ion cur-
rents were stored during a run, and then plotted and digitally printed out in normalized
form at the end of the run.

The GC column temperature was controlled at $-50°$. A stainless-steel
(20 ft. $\times$ 1/16 in. I.D.) Durapak n-octane/Porasil C (100–120 mesh) column was used[7].

Impurities were pre-concentrated and eliminated by passing the helium
carrier gas through a liquid-nitrogen trap before delivery to the chromatograph. The
separation valve between the chromatograph and the mass spectrometer was used to
prevent large volumes of nitrogen and oxygen from the sample from entering the
mass spectrometer.

Procedure

SMF for ambient-air analysis was performed as follows. The sample was
collected in a 10-l glass flask equipped with two toggle valves. The air was drawn
into the sampling flask with an AMC-1 diaphragm-type pump (Shimadzu, Kyoto,
Japan). A 50-ml sample of air from the flask was injected at the GC inlet by means
of a glass syringe. The helium carrier gas (8 ml/min) carried the air on to the head
of the column held at $-50°$. A period of 3 min was necessary for the nitrogen and
oxygen in the sample to pass through the column and to be vented from the
system. In each run, the column temperature was initially maintained at $-50°$ for
15 min, then programmed to $90°$ at $16°$/min.

At the end of each run, the column was allowed to remain at $100°$ for at
least 20 min, so that less-volatile materials could be removed before the next
analysis.

The instrument could nominate the six selected ions for each run. The m/e 85
trace, which gave many peaks of modest intensity over the running time, was
chosen as the reference mass fragmentogram for each run. Five selected ions of serial
mass number were selected for the remainig five channels one by one in a stepwise
manner. Thus, for the first run, the selected ions were m/e 11, 12, 13, 14, 15 and
85; for the next run, the ions were m/e 16, 17, 18, 19, 20 and 85, and so on. The
injections and runs were repeated sequentially, and selected ions over the mass range
m/e 11 to m/e 100 were monitored. In this way, 90 mass fragmentograms were
obtained for one sample and were used to reconstruct the mass spectra.

RESULTS AND DISCUSSION

Survey mass fragmentography

Fig. 1 shows a portion of a mass fragmentogram obtained from the
repetitive injections of 50 ml of air from a street in Tokyo; the m/e values
monitored are 70, 71, 72, 73, 74 and 85. Eighteen charts of this type were obtained
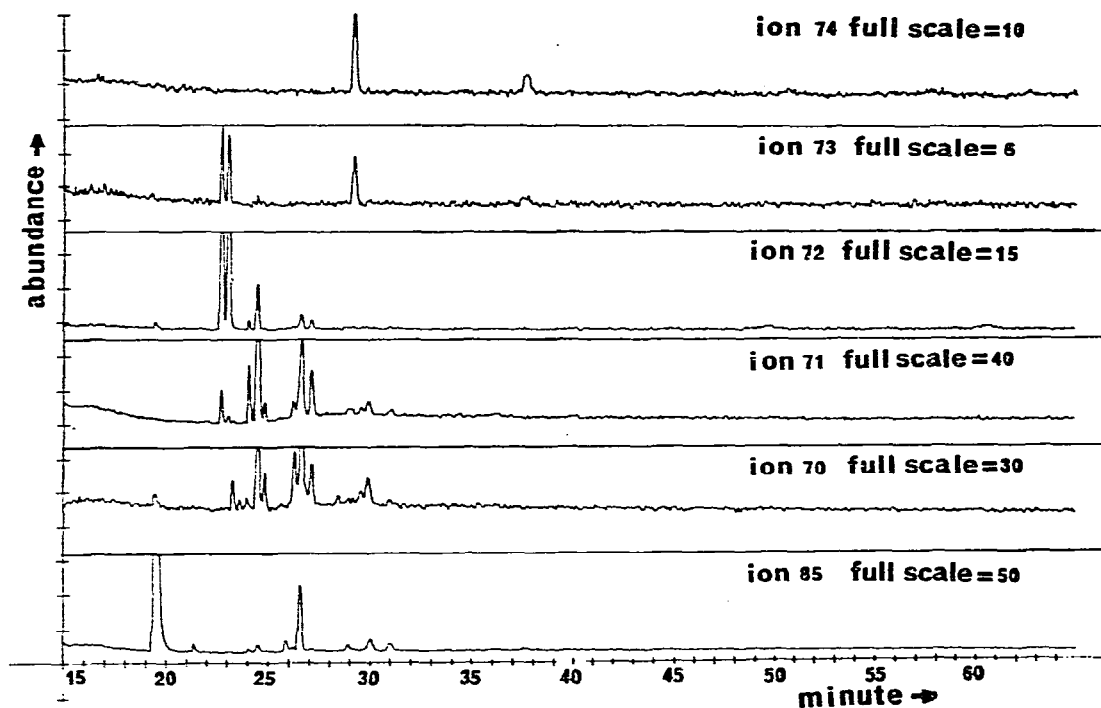in this study. The m/e 18 trace gave a very broad pattern for water elution. The

Fig. 1. Portion of survey mass fragmentogram showing traces for ions m/e 70, 71, 72, 73, 74 and 85.

peaks having signal-to-noise ratios of more than 3 were acquired to reconstruct the mass spectrum for identification; all of them showed clear and distinct separation.

Reconstructed mass spectrum

The reconstruction of the mass spectrum was performed by gathering and arranging mass-fragmentographic peaks of identical retention time. In the upper part of Fig. 2 is shown a reconstructed mass spectrum obtained from the mass-fragmen-
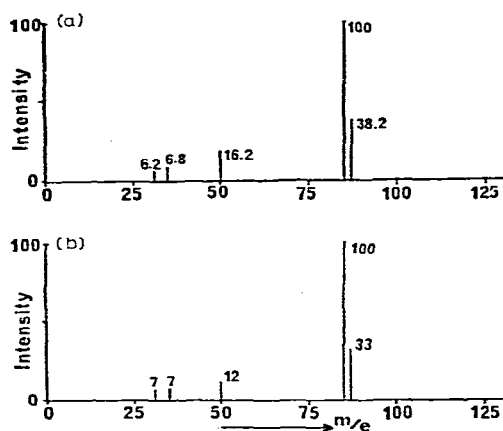

Fig. 2. (a): Reconstructed mass spectrum of dichlorodifluoromethane for the mass range m/e 15–100. (b): Spectrum from published data (ref. 8).

tographic peaks having a retention time of 19.5 min. As the reference mass fragmentogram (m/e 85) showed good reprodicibility, no normalization was necessary. The lower spectrum in Fig. 2 is that of dichlorodifluoromethane cited from a book of mass-spectral data[8]. The identification was performed by comparison of both spectra.

The reproducibility of retention time and of peak height in the repetitive injections is most important in reconstructing a well-qualified mass spectrum from the results of SMF. The retention-time reproducibility defines the reliability of attributing the mass-fragmentographic peaks to a specific compound, and the accuracy of the mass-spectral pattern coefficient depends on the peak-height reproducibility.

Both these reproducibilities were investigated for five replicate analyses (50-ml injection). The retention-time reproducibility was determined from the m/e 85 mass-fragmentographic peak for toluene in the air sample, and the peak-height reproducibility was measured for dichlorodifluoromethane. Both results were satisfactory (see Table I), and the mass-spectral reconstruction could be performed from the survey mass fragmentogram. In a few instances, however, correction for retention-time data using the reference mass fragmentogram was required.

TABLE I

REPRODICIBILITY OF PEAK-HEIGHT AND RETENTION-TIME MEASUREMENTS

Retention time of toluene			Peak height* for dichlorodifluoromethane		
Mean (min)	Standard deviation (min)	Coeff. of variation (%)	Mean	Standard deviation	Coeff. of variation (%)
37.6	0.05	0.13	75.7	8.5	11.2

* In arbitrary units.

Application to urban air analysis

An air sample collected from a street in Ikebukuro (Tokyo) was analysed by using SMF; the compounds identified are listed in Table II. In this study, the complete mass spectrum was not reconstructed for compounds of MW > 100. These compounds, however, were assigned conventionally by mass-fragmentographic identification in comparison with authentic compounds.

Most of the compounds identified are components of automobile-exhaust gas[9], but various oxygen-, halogen- or sulphur-containing species were also detected.

The concentrations of benzene, toluene and xylene were estimated as 30, 53 and 49 ppb, respectively; the estimation was based on comparison of the response of SMF to measured quantities of these compounds.

The m/e 18 trace indicated that the amount of water in a 50-ml air sample that was trapped during the cryogenic condensation was eluted as a broad peak between 23 and 50 min. Interpretation of the reconstructed mass spectrum from these peaks indicated that the amount of water in 50 ml of air was insufficient to affect the fragmentation process[10]. Many mass-fragmentographic peaks other than m/e 18 appeared while water was eluted.

TABLE II

TRACE COMPONENTS SURVEYED AND IDENTIFIED IN URBAN AIR*

Compound	Retention time (min)
Propane	17.6
Carbonyl sulfide**	18.9
Dichlorodifluoromethane	19.5
Isobutane	20.4
n-Butane	20.9
Butene	21.3
Isopentane	22.7
Carbon disulphide	22.9
n-Pentane	23.0
Pentene***	23.3
Pentene***	23.6
Pentene***	23.9
Dimethylbutane	24.0
Methylpentane	24.5
n-Hexane	24.8
Dichloromethane	24.9
Hexane***	25.7
Heptane***	25.9
Dimethylpentane***	26.3
Methylhexane***	26.6
Trichloroethylene	26.9
n-Heptane	27.1
Tetrachloroethylene**	28.8
Octane***	28.9
Benzene	29.1
Methylheptane	30.0
n-Octane	31.0
Toluene	37.6
Ethylbenzene	50.1
o-Xylene	51.8
m-Xylene	52.4
p-Xylene	56.0

* Taken in Ikebukuro, Tokyo, on September 22nd, 1977.
** For these compounds, the mass spectrum cannot be reconstructed completely. Thus, these were confirmed also by retention-time comparison with authentic samples.
*** Structural formula could not be identified.

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