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ANALYSIS OF ORGANIC CONSTITUENTS PRESENT IN DRINKING WATER

J. NOVÁK, J. ŽLUTICKÝ, V. KUBELKA AND J. MOSTECKÝ

Department of Petroleum Technology and Petrochemistry, Institute of Chemical Technology, Suchbátarova 5, Prague 6 (Czechoslovakia)

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SUMMARY

Substances with boiling points up to 140° were stripped from polluted drinking water by bubbling an inert gas through the water. These substances were separated and identified by means of combined gas chromatography-mass spectrometry. The detection limit of this method was two to three orders higher than methods involving the extraction of the same water sample with an organic solvent followed by chromatographic or spectral analyses.

INTRODUCTION

The selection of an appropriate method for the determination of organic substances in water depends on the character of these substances as well as on the amount present.

The qualitative identification of the substances is most frequently achieved by means of gas chromatography, particularly when a mixture of hydrocarbons is present¹⁻³. Spectral methods have so far not found wider application^{4,5} except in special cases, because a complicated mixture is most frequently encountered.

By far the greatest problem in the analysis of organic substances dissolved in water is their low concentration. The direct analysis of aqueous solutions is in most cases impossible¹. Only highly concentrated solutions, such as saline waters from petroleum fields, can be injected directly into the chromatographic column². The detection limit in the gas chromatographic analysis of species dissolved in water is usually increased by extracting them with a suitable organic solvent². Nevertheless, the limiting concentration that can be determined is 0.1 mg/l.

The most effective method for obtaining volatile substances dissolved in water seems to be to strip them from the water with an inert gas^{2,6,7}. With an appropriate experimental arrangement and the use of a flame ionization detector, it is possible to determine one part of the substance in 10¹³ parts by weight of water.

It was our problem to determine the concentrations of organic substances in sources of drinking water.

EXPERIMENTAL

A sample of polluted drinking water was extracted with carbon tetrachloride⁸ and nitrobenzene¹, and the extracts were analysed by gas chromatography-mass

spectrometry (GC-MS). The UV and IR spectra were also recorded for both extracts on a Unicam UV spectrophotometer in a 1-cm cell and a Perkin-Elmer Model 325 spectrophotometer, respectively. A further extraction procedure consisted in bubbling an inert gas through the water. The flow diagram of the apparatus used is shown in Fig. 1. Helium was purified by passing it through the liquid nitrogen-cooled trap into two 250-ml bubblers equipped with coarse frits. The gas from the

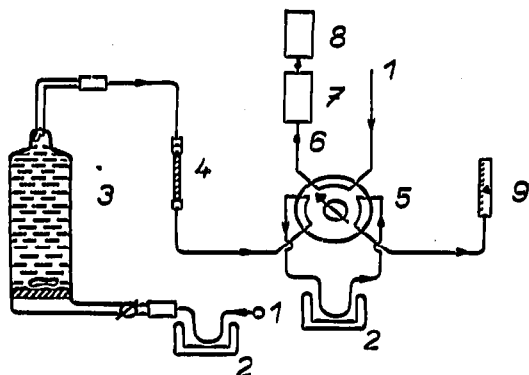


Fig. 1. Flow sheet of the apparatus used. 1 = Source of inert gas; 2 = freezer; 3 = bubbler; 4 = dryer; 5 = six-way cock; 6 = column inlet; 7 = chromatograph; 8 = mass spectrometer; 9 = integrating flow meter.

bubblers was dried over magnesium perchlorate and introduced through a six-way switching valve into a freezing loop (a capillary with I.D. 2 mm and length 50 cm) which was cooled to the temperature of liquid nitrogen and then passed through a flow meter. The injection of the trapped mixture was carried out by rapid heating of the freezing loop to 150° in an oil-bath (pre-heated silicone oil for vacuum pumps). By this method, with the additional use of a salting-out agent (Na_2SO_4), the impurities present in the water were obtained in concentrations that permitted their identification by means of a mass spectrometer combined with a gas chromatograph.

The following conditions were used in the experiments:

| | |
|-----------------------------|-----------------|
| Amount of samples | 2 × 250 ml |
| Amount of salting-out agent | 20 g per 250 ml |
| Flow-rate | 100 ml/min |
| Duration of bubbling | 30 min |
| Temperature | 20° |

The analysis in the combined GC-MS apparatus (LKB 9000) was carried out by using a packed glass column with I.D. 2.5 mm and length 5 m containing 10% of Carbowax 20M on Chromosorb W AW. The flow-rate of the helium carrier gas was about 20 ml/min. The analysis was always carried out with temperature programming from 60° to 200° at 4°/min. The individual components of the mixture, immediately after leaving the chromatographic column and following the removal of the carrier gas in a separator, were introduced directly into the ion source of the mass spectrometer. Approximately 20% of the ionic current, after appropriate amplification, was used for recording the chromatogram. The mass spectrum of each chromatographic peak was recorded. The mass spectra were measured at an

energy of the ionizing electrons of 70 eV and a trap current of 60 μA . The temperature of the ion source was 250° and the pressure was 10^{-6} torr.

RESULTS AND DISCUSSION

In the carbon tetrachloride and the nitrobenzene extract of polluted drinking water we did not detect the presence of any organic substances by the UV and IR spectral methods or by the GC-MS technique.

Only when a gas was bubbled through the sample of polluted drinking water in conjunction with the GC-MS method we were able to separate and determine the organic substances present. The results are shown in the chromatogram in Fig. 2

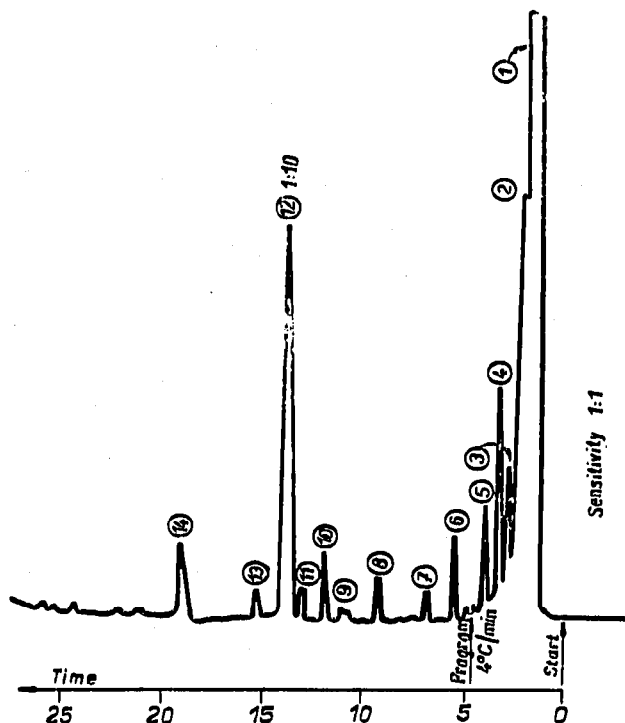


Fig. 2. Chromatogram of compounds present in polluted drinking water. The numbers of the chromatographic waves correspond to those listed in Table I.

and in Table I. The individual compounds were identified by comparison of their mass spectra with literature values⁹. The chromatographic peaks 1, 4, 5, 6 and 14 represent two or more chemical compounds (Table I).

Meticulous attention was paid to all procedures so as to avoid possible contamination of samples from the environment. The preparation and the analysis of the samples were carried out in a well ventilated room, in which no volatile organic substances were handled. For the quantitative determination of the identified components, we prepared a series of standard solutions with concentrations similar to the estimated ones. The standard solutions, prepared according to MELPOLDER *et al.*¹⁰, were then analysed in the same way as the water samples.

The efficiency of the stripping technique in conjunction with the reliability of detection of our recording chain does not differ much for the individual substances identified under our experimental conditions, and is *ca.* $40 \pm 10\%$. When the bubbling time was doubled, the efficiency increased to $55 \pm 10\%$. These data were taken into consideration in the calculation of the concentrations of the substances. Table I therefore gives the actual concentrations of the constituents in the drinking water being analysed.

TABLE I
COMPOUNDS IDENTIFIED IN POLLUTED DRINKING WATER

| Compound | Number of chromatographic peak | Concentration (mg/l) | Catalogue No. (ref. 9) |
|---|--------------------------------|----------------------|------------------------|
| C ₁ -C ₄ hydrocarbons | 1 | $1.2 \cdot 10^{-2}$ | |
| Air + CO ₂ | 1 | N.D. ^a | |
| Pentene | 2 | $5 \cdot 10^{-4}$ | Y 0152 |
| Cyclopentane | 3 | $1.6 \cdot 10^{-4}$ | Y 0116 |
| Cyclopentene and methylcyclopentane | 4 | $3.2 \cdot 10^{-4}$ | Y 0208 |
| Cyclopentadiene | 5 | $3.6 \cdot 10^{-4}$ | Y 0183 |
| Cyclohexane | 5 | $3.6 \cdot 10^{-4}$ | X 0277 |
| Cyclohexene | 6 | $1.3 \cdot 10^{-4}$ | Y 0216 |
| Isobutanal | 6 | | Y 16.44 |
| Tetrachloromethane | 7 | $< 10^{-4}$ | O 1756 |
| Benzene | 8 | $\sim 10^{-4}$ | Y 0603 |
| Trichloromethylene | 9 | | Y 0175 |
| Chloroform | 10 | $9.1 \cdot 10^{-4}$ | Y 0540 |
| Tetrachloroethylene | - | | Y 0604 |
| Toluene | 11 | $< 10^{-4}$ | Z 1083 |
| Dichloroethane | 12 | $6.1 \cdot 10^{-2}$ | W 0003 |
| > C ₇ H ₁₀ | 13 | $< 10^{-4}$ | Z 0225 |
| Xylene (mixture) | 14 | $3.2 \cdot 10^{-4}$ | A 0644 |

^a N.D. = Not determined.

The reliability of the determinations was checked by a number of blank tests in which pure drinking water was used. The results of the analysis of pure drinking water are presented in Fig. 3 and Table II, and show that our experimental procedure detected the presence of benzene and chloroform in drinking water. As the presence of these compounds in drinking water was not likely to occur, we concluded that the contamination of the drinking water with chloroform and benzene took place during the manipulation in the laboratory. In order to confirm this assumption, we performed a number of experiments in which we followed the passage of lower hydrocarbons, trichloromethane and tetrachloromethane from the laboratory atmosphere into freely standing water. We ascertained that these compounds are dissolved in drinking water in concentrations of several parts per million within 1 h.

On the basis of this result it is not possible to give an unambiguous explanation of the origin of the substances present in the water. Absolutely reliable conclusions require the prevention of the contamination of the polluted water being analysed during the entire period of manipulation of the water sample, *i.e.*, from the sampling

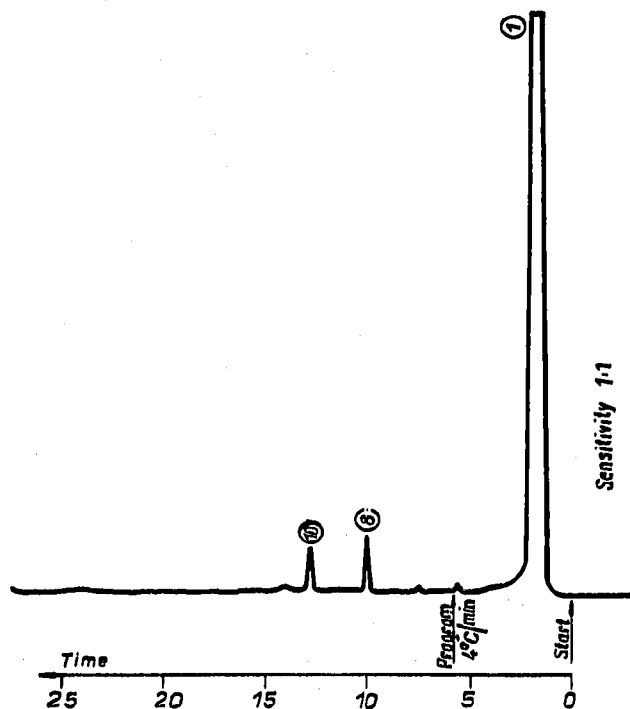


Fig. 3. Chromatogram of compounds present in pure drinking water. The numbers of the chromatographic waves correspond to those listed in Table II.

TABLE II
COMPOUNDS IDENTIFIED IN PURE DRINKING WATER

| Compound | Number of chromatographic peak | Concentration (mg/l) | Catalogue No. (ref. 9) |
|------------|--------------------------------|----------------------|------------------------|
| Benzene | 8 | $\sim 10^{-4}$ | Y 0175 |
| Chloroform | 10 | $< 10^{-4}$ | Y 0604 |

of the water (e.g., in regions subject to emissions from industrial plants) up to the feeding of the sample in to the stripping equipment.

The method described is suitable for determining organic substances dissolved in water at concentrations down to thousandths and ten-thousandths of 1 p.p.m. However, sampling as well as handling and further treatment of the sample necessitate, as already pointed out, scrupulous care in order to maintain high chemical purity, as otherwise distorted results are obtained.

CONCLUSION

On the basis of model experiments we have proved that, as far as the concentrations of the substances to be determined are concerned, the limit of detection

(with the use of the same detection equipment) in the procedure involving bubbling an inert gas through the water is two to three orders higher than methods involving extraction with organic solvents. A limiting factor in the former method is the boiling point of the substances; those which boil considerably above 100° cannot be determined. In such a case, only an organic solvent can be used for the extraction.

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