

CHROM. 7252

## ORGANIC SUBSTANCES IN POTABLE WATER AND IN ITS PRECURSOR

### PART II. APPLICATIONS IN THE AREA OF ZÜRICH\*

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#### SUMMARY

One of the methods described in Part I of this work (transferring organic substances from water at room temperature on to an adsorbent filter by a closed-loop air stream) has been applied to various water samples. These include water from Lake Zürich, taken at different depths and under different weather conditions, as well as relatively pure samples of spring, ground and tap water. In a sample of accidentally contaminated water the degree and the (unexpected) source of contamination have been determined, neither of which could be done by commonly used methods. The characteristics and origin of various water pollutants are discussed and concentrations of selected pollutants are given.

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#### INTRODUCTION

Part I of this work<sup>1</sup> discussed principles and techniques for the identification and determination of organic trace substances in water samples which, as organoleptic and normally used analytical tests do not indicate pollution, are termed potable water. We found that by far the best way to handle the large number of organic substances present in the ppt (nanograms per litre) range was to transfer them via the vapour phase on to a solid adsorbent, from which they are extracted by a solvent.

For stripping the organic substances from water a broad choice of conditions is available, ranging from evaporation by a stream of inert gas at room temperature up to the conditions of steam distillation. The more the nature of the carrier is shifted from a dry inert gas to water vapour, the heavier and more polar the substances that can be determined, while increasing losses of more volatile substances are observed. In this work only the simplest conditions, stripping with air at room temperature, have been employed.

The drinking water of Zürich is mainly pumped from Lake Zürich (approx. 70%), the remainder coming from the ground water streams of the rivers Limmat and Sihl (20-25%) and from a large number of springs (5-10%). As a first application of our method we wished to compare this tap water with its natural precursors.

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\* A more popular report on this work has appeared in *Neue Zürcher Zeitung*, September 10th, 1973.

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## METHODS

*Recent technical improvements*

The following developments were made in the course of routine application of the method previously described<sup>1</sup>.

As stressed already in Part I, it is essential to eliminate any leakage in the closed circuit system used for stripping. The analysis of spring or ground water, for instance, is seriously disturbed by a few litres of ambient air entering the stripping circuit. To ensure that the most critical point, the ground-glass joint on the sample flask, was air-tight we adjusted the flow resistances in the circuit in such a way as to produce a pressure in the headspace of the flask slightly above ambient. Furthermore, we filled the sample flask to a level at which the ground-glass joint is permanently moistened when air is bubbling through the water. Thus a few millilitres of water slowly migrate upstream through the joint, totally preventing any uptake of air in the opposite direction.

The second improvement concerns the extraction of adsorbed substances from the charcoal filter. We found that sufficient desorption (better than 95%) was obtained with a smaller volume of solvent when, before adding liquid carbon disulphide, the charcoal was thoroughly impregnated with carbon disulphide vapour. This was obtained simply by keeping the filter for a few minutes over liquid carbon disulphide under vacuum. Care was taken to avoid any gas stream through the filter producing losses of adsorbed substances.

Most of this work was done using the Metal Bellows pump and the simple installation used is shown in Fig. 1.

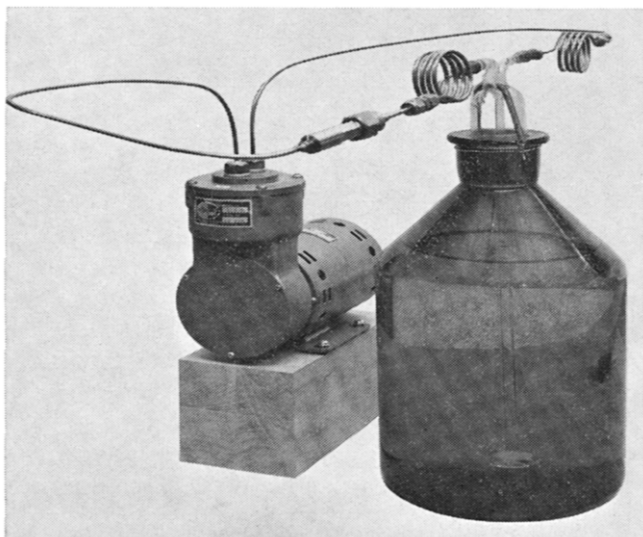


Fig. 1. Equipment for the transfer of organic water pollutants to a small activated charcoal filter. Right: 5-l sample flask. Fused connections between glass and metal parts of closed circuit system and coils for mechanical protection of connections. Left: Model MB 110-10 pump (Metal Bellows, Sharon, Mass., U.S.A.), loop absolutely air-tight, free of greased and plastic parts. A metallic filter holder is shown above and between the pump and the flask.

*Gas-liquid chromatographic analysis of stripped substances*

The volatility range of the organic substances stripped from water is so broad that we were unable to obtain adequate resolution of the whole mixture on one single gas chromatographic column. In this paper we used a compromise with the aim of simplifying the presentation. All chromatograms shown were produced by a Ucon HB 5100 column, which yields the broadest survey of the substances that can be stripped at room temperature. On this column, however, the most volatile substances (overlap region with solvent, benzene, volatile chlorinated hydrocarbons) are not ideally resolved, while heavy substances such as alkanes with more than twenty carbon atoms are lost. Much better results are obtained, for instance, by using a Ucon LB 550 column for the first part of the mixture, and an Emulphor column for the second part. The figures given in Table II have been obtained from two columns, but the corresponding chromatograms are not presented.

*Short description of practical procedure*

The 5-l sample flask is cleaned by prolonged rinsing with tap water. Cleaning with organic solvent, acids or oxidants may lead to artifacts and is therefore not recommended. During filling of the flask, the water should be mixed with ambient air as little as possible. The charcoal filter, containing 1 mg of adsorbent, is cleaned by immersion in carbon disulphide for 30 min; the solvent is renewed three times. An identical treatment is then carried out with *n*-pentane. After rinsing, the filter is transferred to the filter holder without any special drying procedure. The stripping system is assembled and allowed to work for 24 h with an air flow-rate of approx. 2–3 l/min. At the end some sample water should have accumulated above the closed stopper of the flask, proving the absolute air tightness of the system. The filter is put into a tube containing a few millilitres of carbon disulphide, avoiding direct contact between filter and liquid. The tube is evacuated by a water pump; it is closed as soon as the liquid starts to evaporate. After adding the internal standard directly on to the filter disc, the extraction assembly (with cap and sample tube, see Part I) is mounted and extraction by five batches of about 1.5  $\mu$ l each is carried out. Amounts of 2–4  $\mu$ l of the solution are injected for GC analysis. From time to time the filter is extracted once again to check whether the first extraction was complete.

## CLASSIFICATION AND ESTIMATION OF IDENTIFIED SUBSTANCES

Table I gives the names of the major compounds found in water, as identified from their mass spectra —direct coupling with a Varian-MAT Model CH5 mass spectrometer; see Part I. To facilitate this survey of very varied materials, the substances can be classified according to their origin.

*Industrial pollutants*

*Automobile fuel.* Automobile fuel is by far the most widespread material and is found in all kinds of water samples. In most of them it even forms the bulk of the organic material. This is easily seen when the chromatogram in Fig. 4A, which has been obtained from pure water spiked with 0.5 ppb of gasoline, is compared with all the other chromatograms. This ubiquity cannot be explained

TABLE I  
SUBSTANCES IDENTIFIED

No.	Substance	No.	Substance
2	Heptane	75	C <sub>4</sub> -Benzene
8	Octane	76	Dichlorobenzene
9	Benzene	77	Terpene C <sub>10</sub> H <sub>16</sub> O
11	Isononane	78	Dimethylethylbenzene
14	Carbon tetrachloride	79	C <sub>5</sub> -Benzene
18	Trichloroethylene	80	1,2,4,5-Tetramethylbenzene
19	Nonane	81	C <sub>5</sub> -Benzene
22	Isododecane	82	1,2,3,5-Tetramethylbenzene
25	Tetrachloroethylene	83	Terpene C <sub>10</sub> H <sub>14</sub> O
26	Toluene	84	Tridecane
28	Dimethyl disulphide	85	Terpene C <sub>10</sub> H <sub>16</sub> O
34	Isododecane	86	C <sub>4</sub> -Benzene
35	Aminomethylpyridine	87	Terpene C <sub>10</sub> H <sub>16</sub> O
36	Decane	88	Camphor
37	Ethylbenzene	89	C <sub>5</sub> -Benzene
38	2-Methylpentanol-2	90	C <sub>5</sub> -Benzene
39	1,4-Dimethylbenzene	93	Internal standard (1-chlorodecane)
40	1,3-Dimethylbenzene	94	C <sub>5</sub> -Benzene
43	1,2-Dimethylbenzene	97	Tetradecane
44	Isoundecane	98	Trichlorobenzene
47	<i>n</i> -Propylbenzene	101	Cyclocitral
48	Chlorobenzene	102	Caran-4-ol
49	Undecane	105	Naphthalene
50	4-Ethyltoluene	106	Pentadecane
51	3-Ethyltoluene	107	1-Phenyl-2-thiapropane
52	Limonene	108	1-Pentadecene
53	Cineol	110	2-Methylnaphthalene
54	1,3,5-Trimethylbenzene	111	Hexadecane
55	2-Ethyltoluene	112	1-Methylnaphthalene
59	1,2,4-Ethylbenzene	113	Molecular weight 182
60	Isopropyltoluene	116	Dimethylnaphthalene
61	Isododecane	119	Heptadecane
63	Dimethyl trisulphide	120	Diphenyl
64	Propyltoluene	122	1-Heptadecene
65	1,2,3-Trimethylbenzene	123	Diphenyl ether
67	Isobutylbenzene	127	Tri- <i>n</i> -butyl phosphate
68	Dodecane	128	Octadecane
69	Dimethylethylbenzene	129	Acenaphthene
70	Methylpropylbenzene	130	<i>tert.</i> -Butyl acetophenone
72	Dimethylethylbenzene	133	Nonadecane
73	Methylisopropylbenzene	136	Eicosane
74	Methylisopropylbenzene		

by careless handling of gasoline or by accidents. The most important mechanism of contamination seems to be that of evaporation into the atmosphere, from which it is transferred to the water by direct surface contact or, with maximum efficiency, by falling rain. Direct evidence for the latter was found from the study of lake water.

*Solvents.* Solvents such as trichloro- and tetrachloroethylenes, as well as chlorinated aromatic hydrocarbons, are second in importance. If single extraneous

substances are considered, tetrachloroethylene is often found to occur at the highest concentration in natural water. The relatively high levels of chlorinated substances seem to be due to their slow breakdown (see the section on lake water).

*Diesel oil.* Diesel oil and related materials, containing mainly saturated hydrocarbons, do not play any considerable role in organic water pollution in the Zürich area. The chromatogram in Fig. 4c, which is obtained from a water sample artificially contaminated with diesel oil, shows a typical oil pattern which was not observed in any other water analyses. At first, this may be a surprising statement. It is, however, in good agreement with the equally low incidence of saturated hydrocarbons in the atmosphere<sup>2,3</sup>. It seems again that the atmosphere is the most important source of organic water pollution in this area. Besides, the relatively rapid breakdown of *n*-alkanes in water may be a further reason for this finding.

*Various industrial chemicals.* The heavier water pollutants found (not resolved on the Ucon HB 5100 column) were plasticisers, such as phthalate esters and diphenyl ether, at almost constant concentrations. In contrast, dibutyl phosphate and the terphenyls appear in lake water as short-term major pollutants, indicating heavy spillage from an industrial plant.

#### *Substances of natural origin*

*C<sub>15</sub> and C<sub>17</sub> alkanes and alkenes.* These individual compounds are always present as major constituents in water with high microbiological activity during summer. In cold surface water, as well as in ground and spring water, they are present in negligible concentrations. According to Blumer<sup>4</sup> there are specific algae, each of which produces the *n*-alkane and the 1-alkene with a specific carbon number, namely 15, 17, and 23. Not having been able to detect the C<sub>23</sub> pair, we assume that the corresponding type of alga is not present in this area.

*Terpenes.* Terpenes of any functionality (hydrocarbons, aldehydes, ketones, alcohols; in the selected spectrum with ten carbon atoms only) are present in all surface waters, though not in important concentrations. We have good evidence indicating that their biological breakdown is very effective. In many cases we are able to deduce a typical terpene character from the mass spectra, but not the exact structure. Even the individual terpenes listed in Table I have to be considered as tentative identifications.

*Sulphur compounds.* The presence of sulphur compounds (dimethyldisulphide, dimethyltrisulphide and 1-phenyl-2-thiapropane) in warm surface water presumably indicates the anaerobic breakdown of proteins; they can possibly be considered as indicators for faecal material.

#### *Unidentified substances*

There are many substances, even relatively important ones such as Nos. 104 and 113, the mass spectra of which are very difficult to interpret. They are not derived from common industrial chemicals but rather from natural products. Their relative importance increases with decreasing volatility.

In most samples we find, furthermore, a series of homologous substances (broad tailing peaks close to peaks Nos. 34, 47, 65, 80, 96, 105 and 110). The typically poor peak symmetry points to a polar structure, so far unknown. The odour of the concentration of these substances shows a striking correlation with

the typical waste water odour, which is often released by the extract solution, even when the latter is obtained from an odourless water sample.

#### *Substances not detected by our method*

We wish to stress again that there are organic water pollutants which occur in larger amounts than do all the substances mentioned above, but which are not detected by our procedure *e.g.* detergents, many kinds of acids (as humic acids and amino acids), carbohydrates and urea. The vapour pressures of all these strongly polar substances over their aqueous solutions are too low to allow evaporation from the water.

#### *Quantitative estimation*

Table II gives the average concentrations for some selected substances in different water samples. The corresponding technique has been described in Part I. We spiked purified water with known amounts of all the selected substances. This allowed us to determine the respective recoveries obtained under identical stripping conditions. The peak areas in chromatograms from natural samples were then corrected to 100% recovery.

TABLE II

CONCENTRATIONS OF SELECTED ORGANIC COMPOUNDS IN VARIOUS WATER SAMPLES, AS DETERMINED IN OCTOBER 1973

<i>Compound</i>	<i>Concentration in ppt (ng/l)</i>				
	<i>Lake surface</i>	<i>Lake 30 m</i>	<i>Spring</i>	<i>Ground</i>	<i>Tap</i>
Benzene	28	22	18	45	36
Trichloroethylene	38	65	5	80	105
Tetrachloroethylene	140	420	12	1850	2100
Chlorobenzene	3	12	—	14	6
Dichlorobenzene	16	26	—	—	4
Trichlorobenzene	6	42	—	—	4
Camphor	12	2	2	—	2
Naphthalene	8	52	—	—	8
Pentadecane	16	4	2	2	4
Heptadecane	20	4	1	—	3
Diphenyl ether	48	8	—	3	3
Tributyl phosphate	82	54	—	10	14
Gasoline (mixture)	~ 2000	~ 100	~ 50	~ 800	~ 800
Diesel oil (mixture)	~ 100	< 50	< 10	< 50	< 50

#### LAKE WATER

Figs. 2B and 2C clearly show automobile gasoline to be the most important organic pollutant. It is interesting, however, to compare Fig. 2B with Fig. 4A, obtained from gasoline-spiked water. While in the xylene area (peaks 39, 40, 43) both chromatograms show similar amounts, the heavier gasoline components (*e.g.*,

79–82) appear at five times the concentration in Fig. 2B. In other words, the distribution of gasoline components in the lake, as compared to the original distribution, is strongly modified in favour of the heavier substances. This is not surprising, as the transfer from the atmosphere to the water increases with decreasing volatility of substance.

A further difference between authentic gasoline (Fig. 4A) and gasoline in lake water (Fig. 2B) is the following. Ethylbenzene (37) in the lake is reduced to about one tenth of its original concentration. The same effect, although less pronounced, occurs with *n*-propylbenzene (47). It seems that longer side chains on the benzene ring enhance breakdown of substances. It is important to note that this observation is made under summer conditions with high biological activity in the warm water and with reduced supply of volatile gasoline components from the atmosphere. We have never observed this modified distribution of the xylenes when the temperature of the water was below 20°.

This explanation finds further confirmation when Figs. 2B and 2C are compared. Heavy rain during one night washed out the gasoline vapour from the atmosphere. Thus, the next morning (Fig. 2C) we found that the gasoline constituents had approximately doubled, while ethylbenzene and *n*-propylbenzene (37, 47) had increased about ten-fold and five-fold, respectively. This shows that the above-mentioned modified distribution occurs in the water, not in the atmosphere.

The best evidence pointing to the atmosphere as the most important source of the heavy gasoline content in the water is the following. The gasoline content had been approximately doubled by the rainfall, whereas other substances not found in the atmosphere did not change in concentration. These include, for instance, the chlorinated aromatics 76 and 93, the terpenes 52, 77, 87 and the industrial chemicals 123, 127, 130. All these substances must have been introduced into the lake by rivers or water pipes; some of them (certain terpenes) may have been biologically synthesised in the lake water. We have, however, no explanation for the obvious increase of the C<sub>15</sub> and C<sub>17</sub> alkanes and alkenes, caused by the rainfall.

The chromatogram in Fig. 2A was obtained from the main water supply of the City of Zürich, which is taken at a depth of 30 m at the same location where the water of the chromatograms in Figs. 2B and 2C had been sampled. Surprisingly, about twenty times less gasoline was found than in the surface samples taken from a vertical distance of only 30 m away. The gasoline found shows almost the original composition. The gasoline content is even lower than in our purest spring and ground water samples. We do not feel at all competent to comment on this observation, as we have no information from where and in which way this water had been transported to the position where we sampled it. We may add, however, that for another lake in our area we have found a similar decrease of gasoline content with increasing distance from the surface.

The next striking observation is that the most important pollutants of this sample (18, 25, 76, 98) are chlorinated hydrocarbons. At the surface, where the overall organic pollution is much higher, the same substances appear in much lower concentrations. One is tempted, of course, to explain this by great differences in the rate of breakdown for certain organic groups.

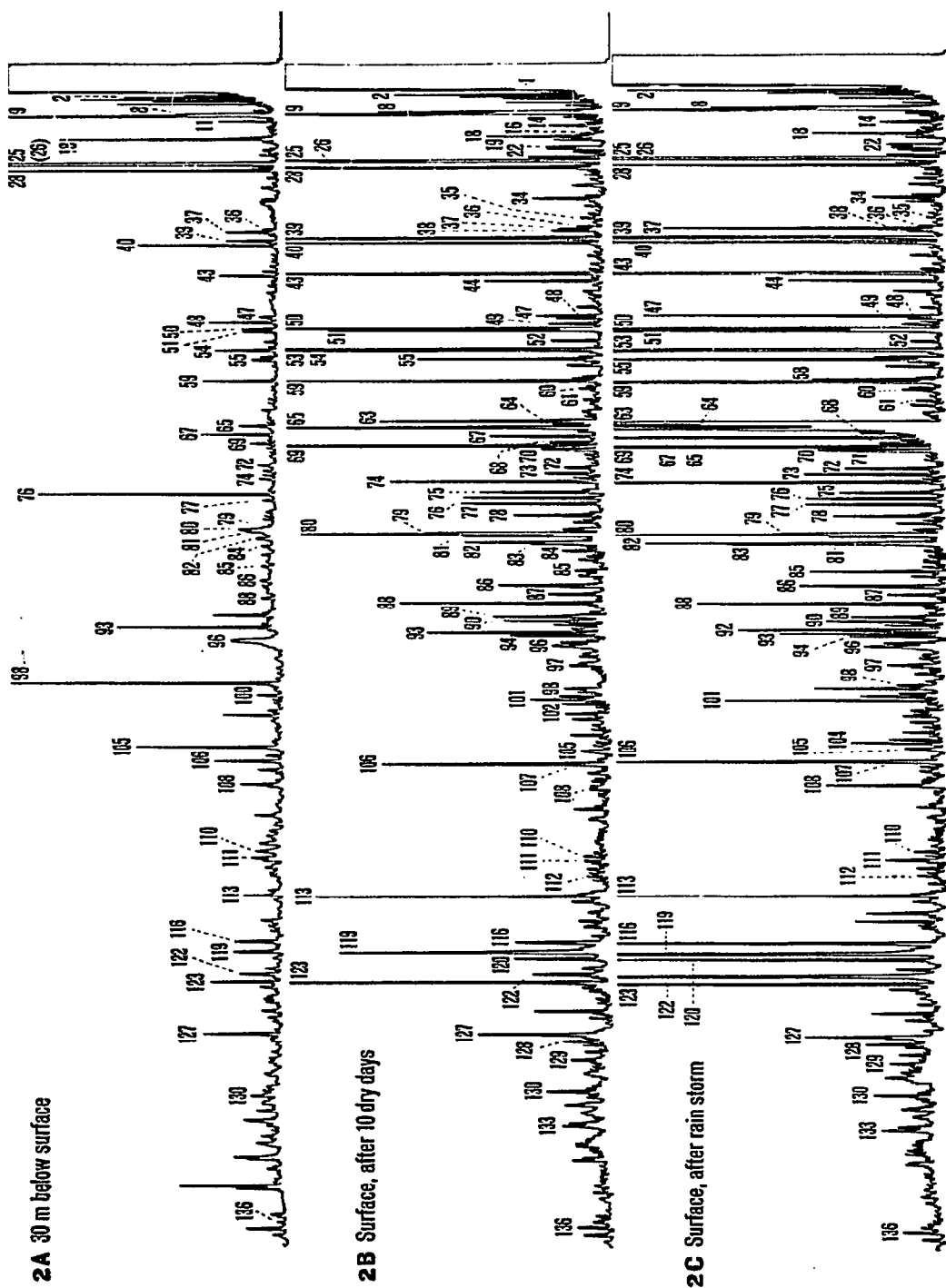


Fig. 2. Gas chromatograms from water samples taken in July 1973 at the same location, but at different depths, or under different weather conditions, from Lake Zürich. Chromatographic conditions: glass capillary column, 120 m  $\times$  0.32 mm, coated with Ucon HB 5100; hydrogen carrier gas at a flow-rate of 4.5 ml/min. A 4.0- $\mu$ l amount of carbon disulphide solution was injected into the column at room temperature and the split valve closed for 30 sec. The temperature was programmed at 1.5°/min from 25° to 175°. The Model GI flame ionization detector,  $\times$  8 was from Carlo Erba, Milan, Italy.



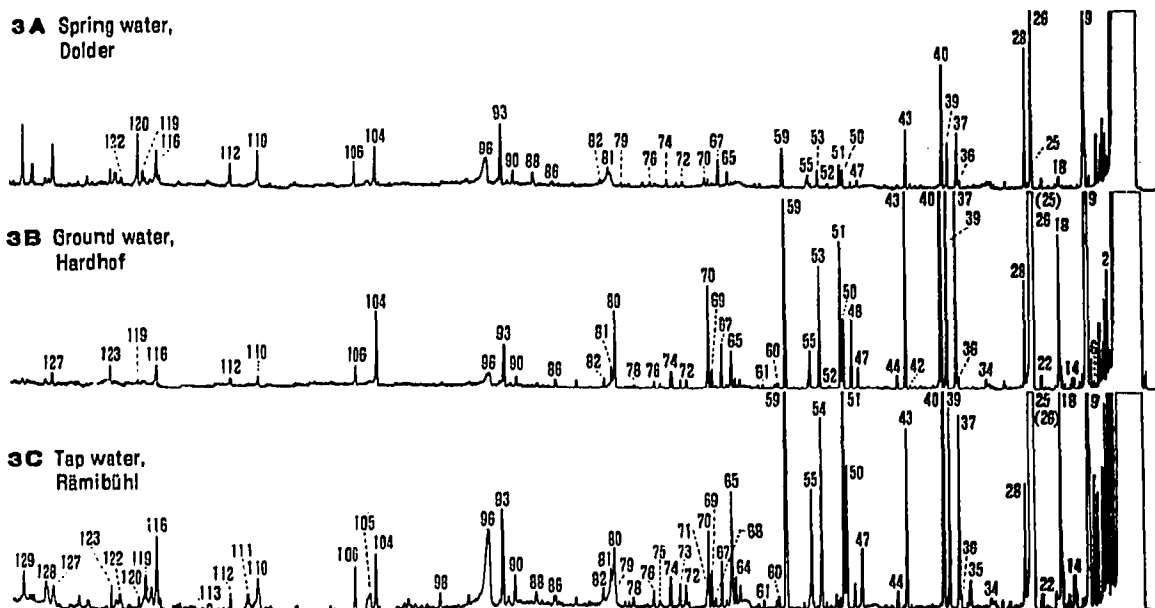


Fig. 3. Analysis of relatively pure water samples. Conditions as in Fig. 2.

#### SPRING, GROUND AND TAP WATERS

The spring water, yielding the chromatogram in Fig. 3A comes from a hill near the city, which is mainly covered by forest and not populated. The water sample is one of our rare ones containing almost nothing other than gasoline. Some of the heavier substances (110, 112, 120) are probably derived from the internal surface treatments of some pipes. The mass spectra of the remaining substances are complex. Most of them suggest terpenoid structures. As we know from earlier investigations<sup>3</sup>, the hill is surrounded by atmospheric gasoline vapours. The surface water entering the soil of the hill should, therefore, not differ strongly from the surface water of the lake, as far as the gasoline content is concerned. Taking this into account, we must consider that the natural filtration process yielding the water quality found in Fig. 3A is very efficient, though not perfect. This interpretation is supported by the fact that all naturally filtered water samples (*i.e.*, spring and ground water) show an internal distribution of gasoline constituents modified in favour of the more volatile substances, which is an opposite observation to that made on the surface water of the lake. The explanation may simply be that the heavier gasoline constituents are more strongly adsorbed to the soil particles, while the lighter ones pass through the filter layer in relatively greater amounts. When considering details of this kind it is necessary to remember the extremely low absolute concentrations indicated in Table II.

The ground water, yielding Fig. 3B, passes a densely populated and partly industrialised area before it is pumped and mixed with lake water to give the drinking water of the City of Zürich. It is not surprising, therefore, that it contains three times more gasoline than the spring water. In addition, it also contains much more chlorinated material (18, 25, 48). A less expected result may be the somewhat greater

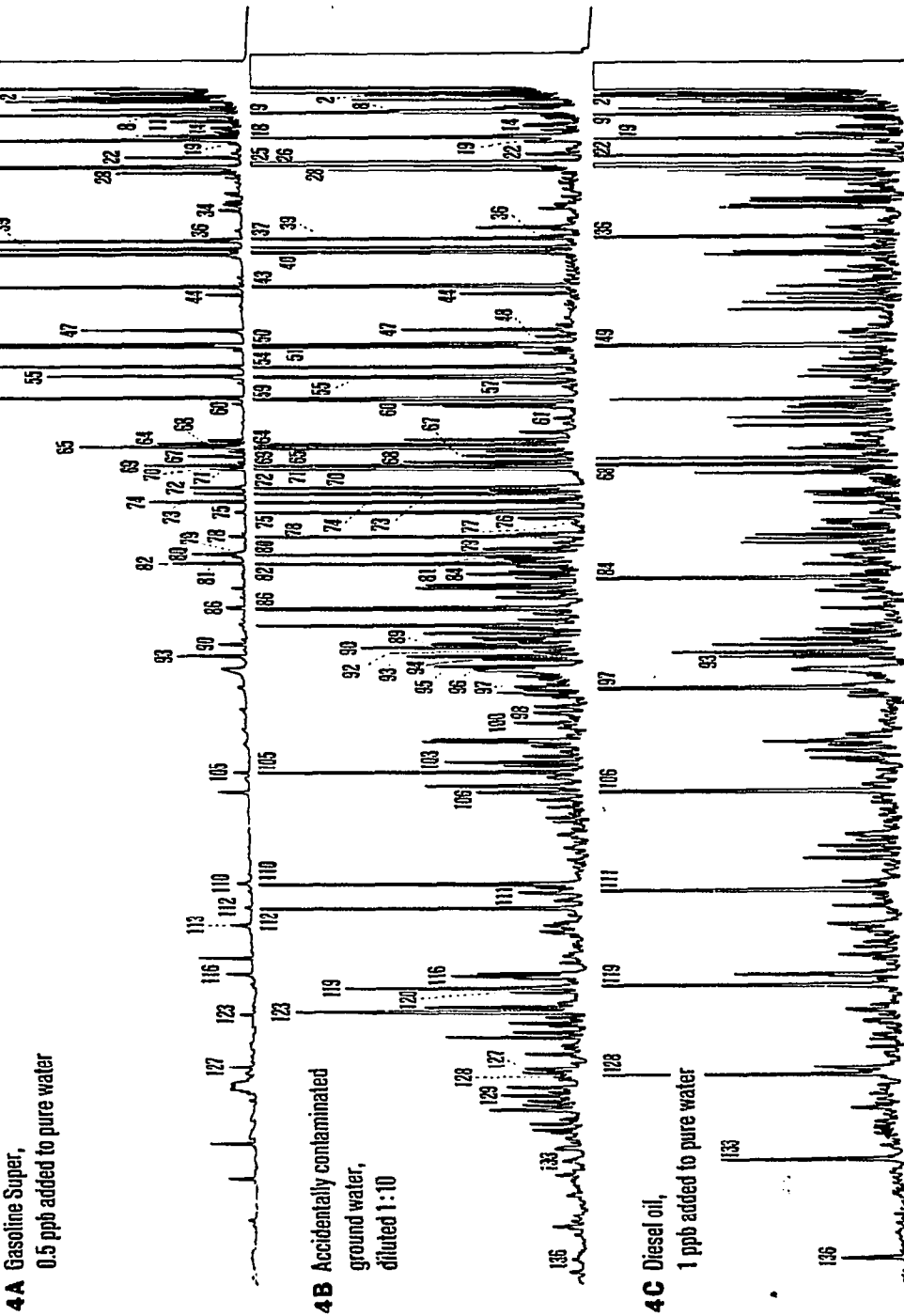


Fig. 4. Comparison of an accidentally contaminated water sample (B) with pure water spiked with known amounts of gasoline (A) and diesel oil (C). For direct quantitative comparison the peak areas in B have to be increased ten times to compensate for the 1:10 dilution. Note the exact coincidence of peaks in A and B, but almost no coincidence between B and C. A and C are also used as calibration runs for the estimation of gasoline and diesel oil mixtures, respectively.

concentration of organic pollutants in the ground water, as compared to that in lake water sampled 30 m below the surface.

While spring and ground water were sampled untreated, *i.e.* before any artificial purification, the tap water (Fig. 3C) had passed several purification procedures. On the other hand, it may have taken up additional pollutants from the pipe system. To reduce this latter influence to the minimum, we had the tap, from which the sample for Fig. 3C was taken, continuously running for several weeks. The tap water shows, nevertheless, slightly more pollution than its untreated precursors. Again we do not feel competent to discuss the meaning and the origin of individual substances, among which the unidentified homologous series of polar substances (Nos. 64, 80, 96, 105, 110, 119) may be of special interest.

#### EXAMPLE OF ACCIDENTAL GROUND WATER POLLUTION

We report this example to show what can be done by our method and, especially, how much more can be done than by the commonly used methods.

In a Swiss community 20,000 litres of Diesel oil had been spilled into the soil over the path of an important ground water stream. The local authorities acted by efficiently pumping out the ground water at the location of the accident. After half a year of continuous pumping the experts were no longer able to taste or smell any contamination. At the same time the commonly used IR method reached its detection limit. Thus no further information, either subjective or objective, on the contamination was available. When we first tested the water, our equipment became so heavily overloaded that it took three days to eliminate the memory effect. From a sample diluted ten times we obtained a reasonable analysis (Fig. 4B). To our great surprise, however, the contamination was obviously gasoline, not diesel oil as expected. Besides the excellent qualitative agreement between Figs. 4A and 4B a further important observation can be made. While in the xylene area (around 40) the concentrations in both samples are similar, the concentrations in Fig. 4B show a rapid relative increase with decreasing volatility of substance. Naphthalene (105), for instance, occurs in 4B at almost twenty times the level in Fig. 4A. We think that this indicates an old gasoline contamination. The low-molecular-weight substances, which are less adsorbed on the soil particles, have been eluted more effectively than the heavy ones, with the effect that the latter appear relatively enriched. Thus the example shows that our method is much more sensitive and, in addition, yields detailed information on the kind of contamination.

#### ACKNOWLEDGEMENT

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