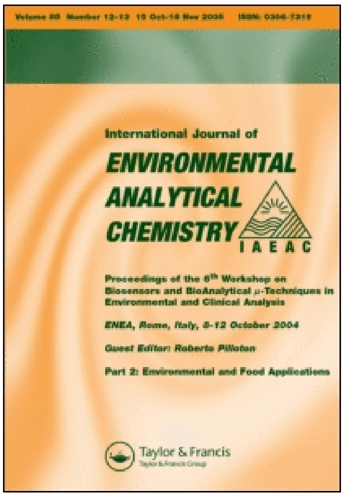


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Inorganic Compounds and Organic Acids in Different Types of Water by Ion Chromatography

R. Schwabe[a]; T. Darimont[a]; T. Möhlmann[a]; E. Pabel[a]; M. Sonneborn[a]
[a] Institute for Water, Soil and Air Hygiene, Federal Health Office, Berlin 33, F.R.G.

To cite this Article Schwabe, R. , Darimont, T. , Möhlmann, T. , Pabel, E. and Sonneborn, M.(1983) 'Determination of Inorganic Compounds and Organic Acids in Different Types of Water by Ion Chromatography', International Journal of Environmental Analytical Chemistry, 14: 3, 169 — 179
To link to this Article: DOI: 10.1080/03067318308071617
URL: http://dx.doi.org/10.1080/03067318308071617

Intern. J. Environ. Anal. Chem., 1983, Vol. 14, pp. 169–179
0306-7319/83/1403-0169 $18.50/0

Determination of Inorganic Compounds and Organic Acids in Different Types of Water by Ion Chromatography†

R. SCHWABE, T. DARIMONT, T. MÖHLMANN, E. PABEL
and M. SONNEBORN

Institute for Water, Soil and Air Hygiene, Federal Health Office, Correnspiatz 1, D-1000 Berlin 33, F.R.G.

(*Received June 7, 1982*)

In recent years, the authors studied, by means of ion chromatography, different drinking, surface and rain waters for their inorganic ingredients such as chloride, fluoride, nitrate, phosphate and sulphate. The results of measurements in drinking water samples from the entire territory of the Federal Republic of Germany exceeded limiting values especially in the cases of nitrate and sulphate. Determination of the anionic composition of various surface waters sampled in the Federal Republic revealed a considerable variation of the individual parameters. Measurements in rain water exhibited seasonal variations. The potential for a determination of organic compounds in water has been examined for carboxylic acids as an example.

KEY WORDS: Ion chromatography; water pollutants; surface water; drinking water.

INTRODUCTION

One of the main environmental problems is the pollution of water by inorganic and organic compounds; they influence the quality of upgraded water and can cause health risks. Therefore an analysis of water is highly necessary, and it is useful to apply a method that enables the determination of more than one interesting compound simultaneously.

---

†Presented at the 12th Annual Symposium on the Analytical Chemistry of Pollutants, Amsterdam, April 1982.

Regarding the inorganic compounds in water it can be recognized that the inorganic compounds chloride, fluoride, nitrate, sulfate and phosphate are of great importance for checking the water quality. Therefore ion chromatography has beeen applied more and more in recent years.[1] This method has two important advantages: The determination of the compounds of interest within a short time (approximately 20 min for one sample) and automatization for routine work are possible.

Type :	**Dionex D 12**
Sensitivity :	**1 kS [Ω^{-1}]**
Analytical Column :	**Fast Run Anionen Separator**
Suppressor Column :	**Anionen Suppressor**
Sample Loop :	**100 µ l**
Pump Flow :	**115 ml/h**
Pressure :	**22 barr**
Runtime :	**11 min / sample**
Eluent :	**0,0048 mol / l Na HCO_3** **0,0023 mol / l Na_2CO_3**

FIGURE 1 Conditions of ion chromatography.

TABLE I

Concentration range of anions in different types of water

		Drinking water	Surface water	Meteoric water
$F^{\ominus}$	mg/l	<0.1–3	<0.1–1	<0.1–0.4
$Cl^{\ominus}$	mg/l	<0.5–454	32–7200	1–6(20)
$PO_4^{3\ominus}$	mg/l	<0.5–10	<0.5–25	<0.5–3.5
$NO_3^{\ominus}$	mg/l	<0.5–370	<0.5–64	<0.5–12
$SO_4^{2\ominus}$	mg/l	<0.5–1200	44–780	6–20(73)

Drinking water, surface water and rain water were investigated by ion chromatography with regard to their contents of chloride, flouride, nitrate, sulfate and phosphate. The conditions of ion chromatography are listed in Figure 1; Table I shows the range of concentrations in the different types of water.

Rain water has the lowest pollution; drinking water has a higher amount of the determined anions, and surface water shows the highest pollution. The widespread concentration range for chloride in the different types of water and the high concentrations for sulphate and nitrate in drinking water are striking.

RESULTS AND DISCUSSION

Drinking water

About 850 samples of drinking water from the Federal Republic of Germany were investigated.

Figure 2 shows in the upper part the presentation of the 90-percentile (90% of all samples have a lower amount than the shown value; 10% have a higher amount) and the median values. In the lower part of the figure there is a comparison between these values and the MAC (Maximal Admissible Concentration) and the GL (guide level) given in the "Directive for Drinking Water of the European Community".[2]

For chloride only a value of 25 mg/l is recommended, 55% of the samples have a content higher than the recommended value. This may result from the usage of salt for urban deicing in winter, and from geological conditions of the soil.[3] For flouride the value of the MAC is 1.5 mg/l; 0.6% of the samples have a higher content.

The MAC for nitrate is 50 mg/l; 25 mg/l is the value of the GL. 5% of the samples are above the MAC, but 14% of the samples have higher concentrations than given by the guide level. A reason for these high amounts can be the use of fertilizers in agricultural areas.[4,5]

For phosphate very low concentrations were determined. The guide level of 0.54 mg/l was exceeded by 12% of the drinking water samples and the Maximal Admissible Concentration of 6.7 mg/l by 0.4%. Very high values for phosphate in drinking water can be caused by fertilization over the average level or by waste water polluted by phosphate compounds.[3]

Contrary to this the sulphate concentrations are very high. 2% of the samples are above the MAC of 250 mg/l, but 62% are above the recommended GL of 25 mg/l. Reasons may be the geological structure of the soil, the so called "acid rain" and the unloaded ashes of brown coal used in power plants for the production of electricity.[6,7]

Rain water

Over a period of a year rain water was collected in different areas of Berlin and measured; Figure 3 shows the results for chloride, fluoride,

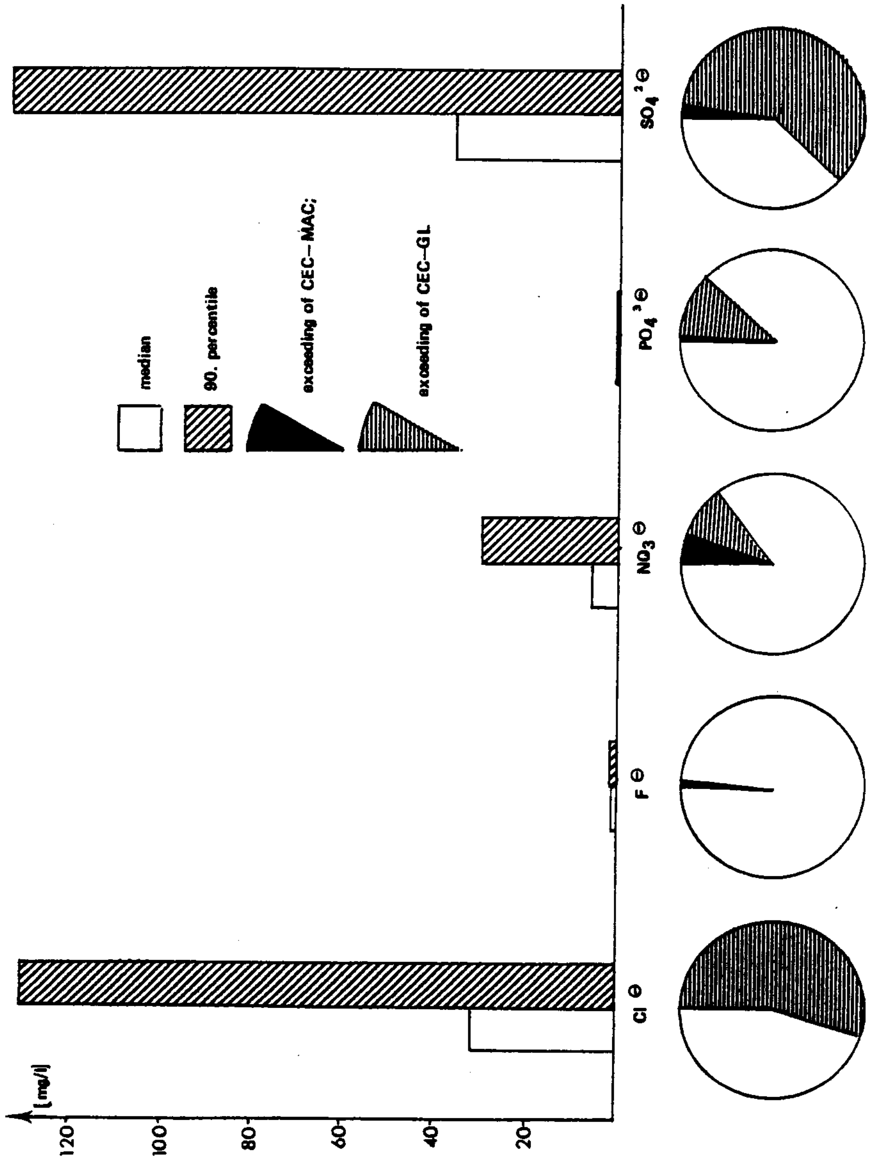


FIGURE 2 Anionic composition of various drinking waters of the total FRG.

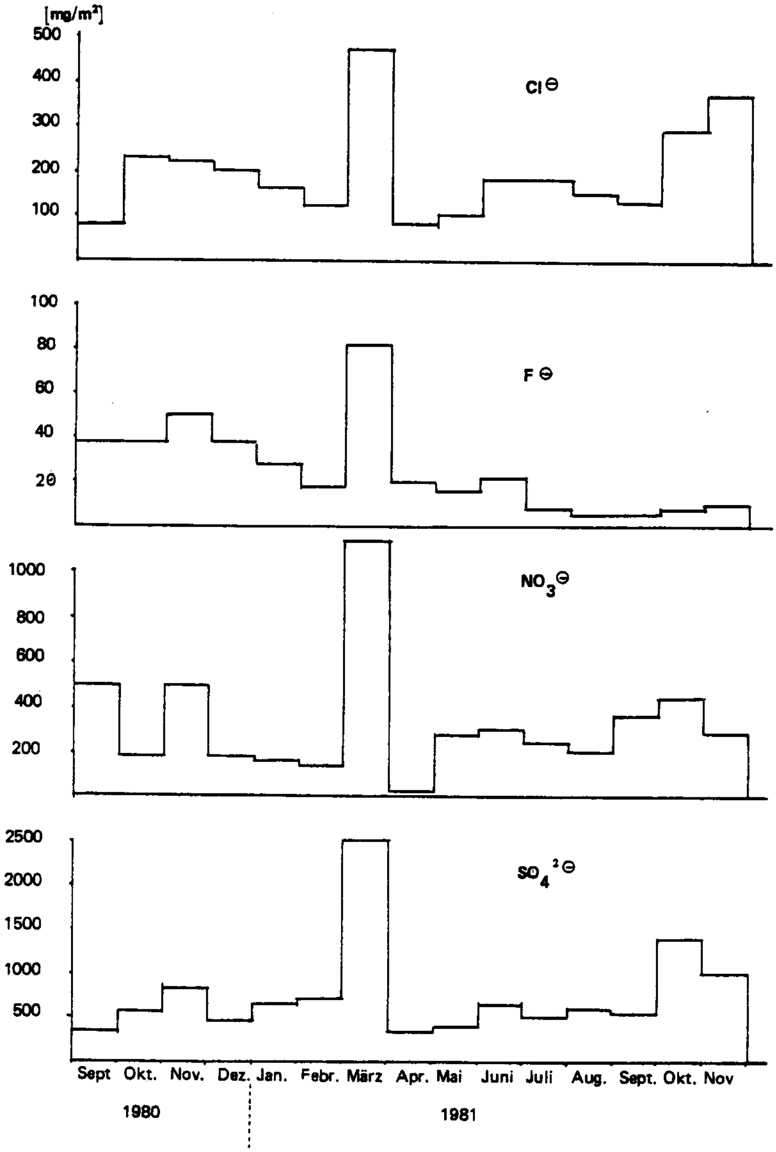


FIGURE 3 Rain water (Berlin-Marienfelde).

nitrate and sulphate. The month of March shows significantly higher loads than the other months, caused by a lot of rainfall in Berlin in March.

There is also a high load of sulphate and nitrate for the months of October and of November. There may be a connection between the

Autumn rainfalls and the beginning of the heating period in Berlin. Still a large number of flats have coal firing in Berlin. Further investigations for the explanation of all effects are necessary.

For chloride, about 4 g/m^2 are falling down with the rain on the ground. For nitrate, fluoride and sulphate 3.8 g/m^2; 0.5 g/m^2 and 9.8 g/m^2 were found respectively.

Surface water

From the river Lippe eight samples were taken and the compounds nitrates, sulphate and chloride were determined by ion chromatography. The lower part of Figure 4 shows the course of the river and the places where the samples were taken; in the upper part of Figure 4 the corresponding concentrations of sulphate, nitrate and chloride are listed.

The concentrations determined near the city of Hamm increase during the following course of the river; the reason for the high contents found nearby the city of Ahsen, is a big industrial area ("Ruhrgebiet") south of the river Lippe with many small rivers going up to the Lippe. The content of nitrate decreases now in the following course, but is high again in Wesel. There is an influence from the higher polluted river Rhine.

The sulphate and chloride concentrations have the tendency to increase during the course of the river. In Wesel the concentrations for these two compounds are more than twice those at the beginning near the city of Hamm.

The river Weser was also investigated. The course of the river and the places where the samples were taken are drawn in the middle of Figure 5. The concentrations are listed in the small figures, numbered according to the places where the samples were taken.

In the river Fulda (point 1) low concentrations, except for nitrate, were found. In the river Weser there is just the opposite result; high pollution except for nitrate. So the river Weser shows in point 3 a high pollution for all five compounds determined. The river Werra runs through an industrial area of the German Democratic Republic, and the uptake of the pollution occurs in this area.

The pollution rates in the places 4, 5 and 6 do not change significantly; there is an increase in nitrate and higher concentrations for fluoride. In point 7 (river Aller) a high increase in nitrate again and a very low amount of chloride was found. The content of chloride remains nearly on the same level up to the estuary of the river (point 9). Much more chloride was expected because of the chloride content in sea water. Very low contents of nitrate and phosphate were determined, at point 9, although there had been high concentrations at points 8 and 7.

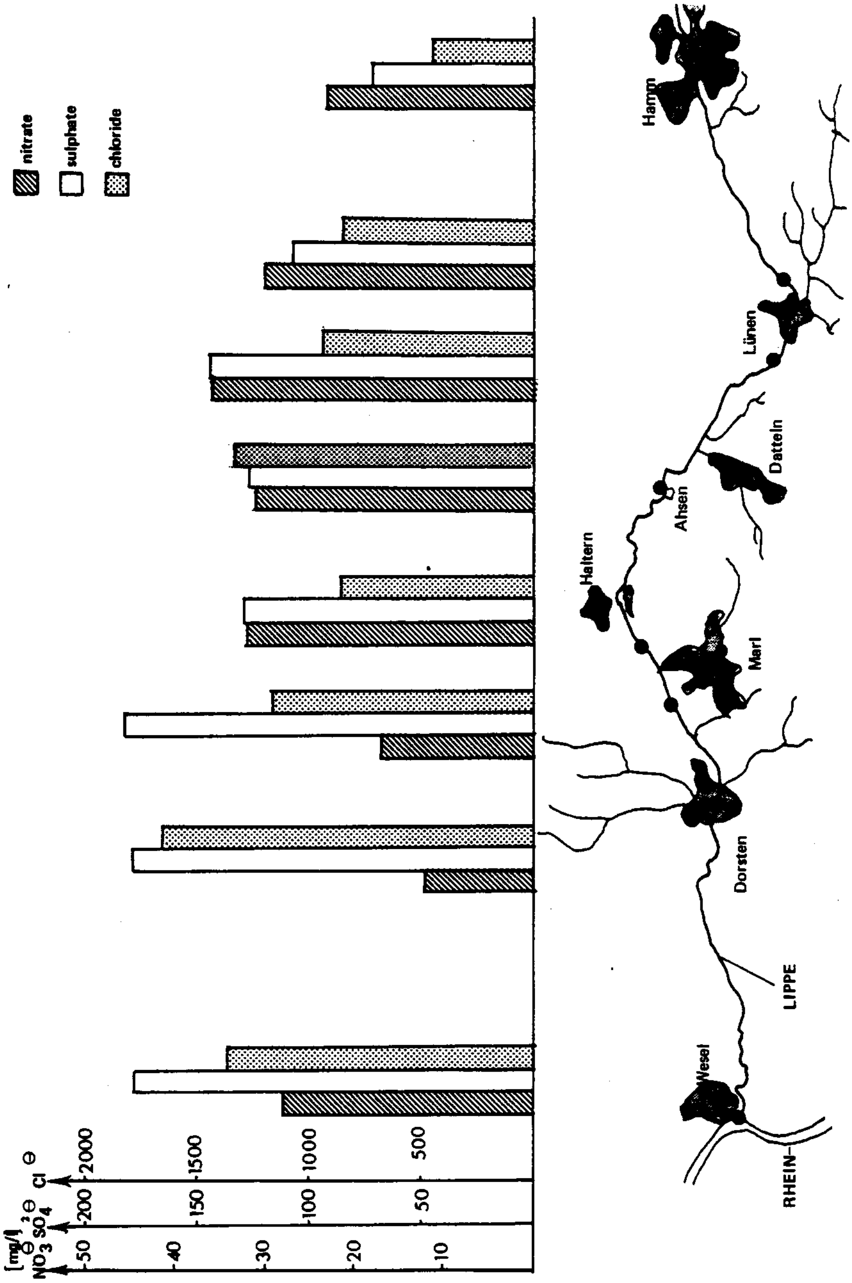


FIGURE 4 Anionic pollution of the river Lippe (F.R.G.).

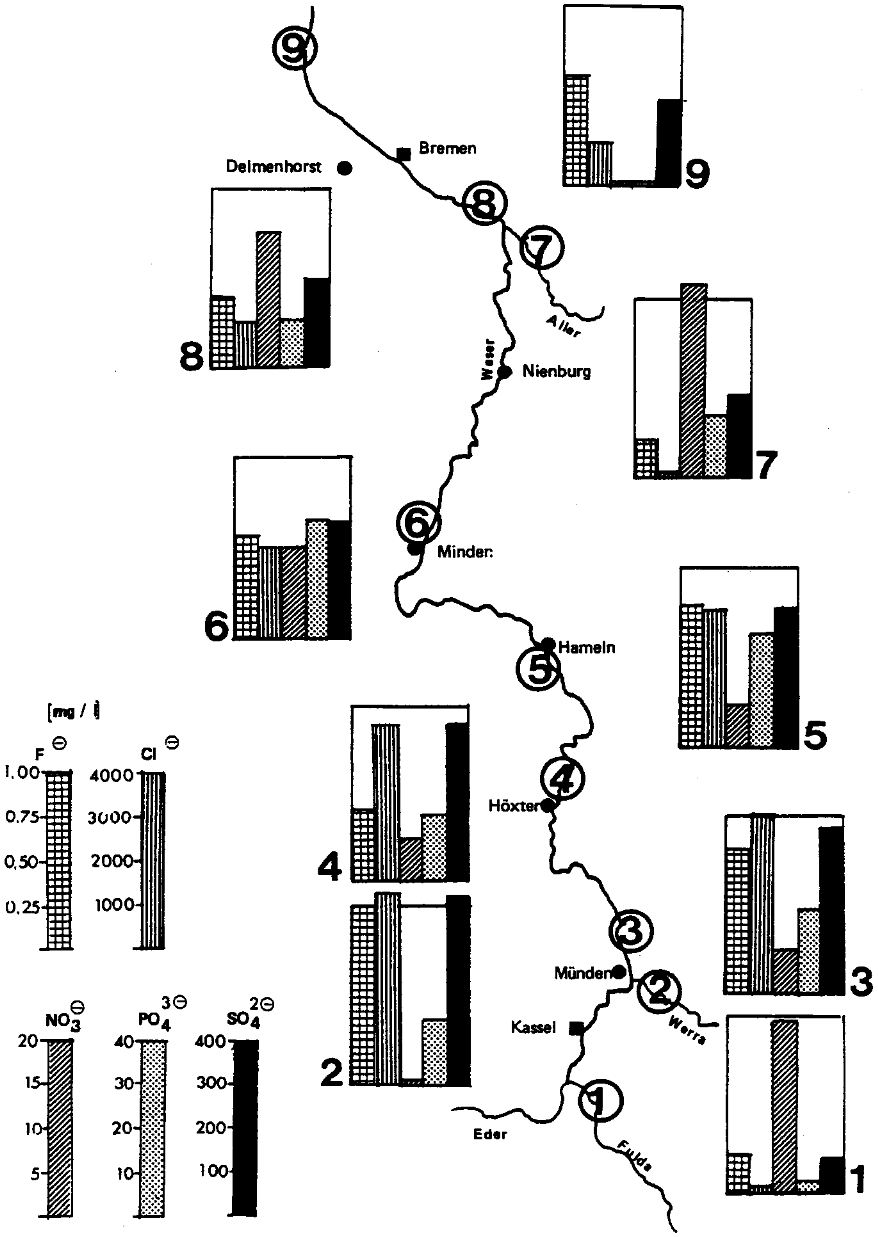
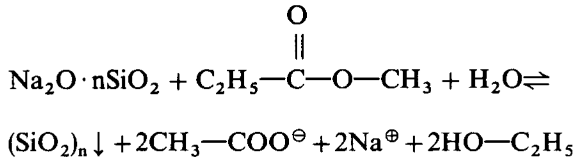


FIGURE 5 Anionic pollution of the river Weser.

Organic compounds

The chemical consolidation of soils by injection of silicate gels is a technique which has increased in scale and importance since its introduction in 1925. These techniques work on the basis of an injection of silicate solutions and precipitants. In cohesiveless, granular soil formed by sands of fine to intermediate grain, the application of such techniques will result in a compaction with a simultaneous increase in shear-strength and the sealing of interstices.

In the course of a research program the quality of ground water nearby an underground engineering building site was checked; for consolidation of the underground sodium silicate solution had been injected. This process is described by the following equation:[8]



$$Na_2O\cdot nSiO_2 + C_2H_5{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3 + H_2O \rightleftharpoons$$

$$(SiO_2)_n\downarrow + 2CH_3{-}COO^{\ominus} + 2Na^{\oplus} + 2HO{-}C_2H_5$$

The ethyl acetate set free by this reaction can be determined by ion chromatography. The temporal and regional distribution of this pollutant gave information about the extent of influence on the ground water.

After preliminary experiments the separation of fluoride, chloride, and acetate was also possible in the waters to be checked. More experiments about the detection and separation of organic micropollutants now seem to be necessary. For this the group of carboxylic acids were investigated as an example. Up to now the separation and detection of fumaric acid, succinic acid/adipic acid and oxalic acid is possible (Figure 6).

One of the main problems of the detection of carboxylic acids in water is the low concentration of these compounds. So enrichment of the water samples will be necessary before the injection of the sample. Different types of ion exchangers and resins were tested for this purpose, but up to now no agreeable results were found.

CONCLUSION

For checking the water quality it is necessary to carry out an analysis. For inorganic compounds this can be done by ion chromatography; more than one parameter can be determined simultaneously. The method is suitable for automation, and the runtime for one sample is about 10 min. The determination of organic micropollutants in water by ion chromatography is still in the experimental development state.

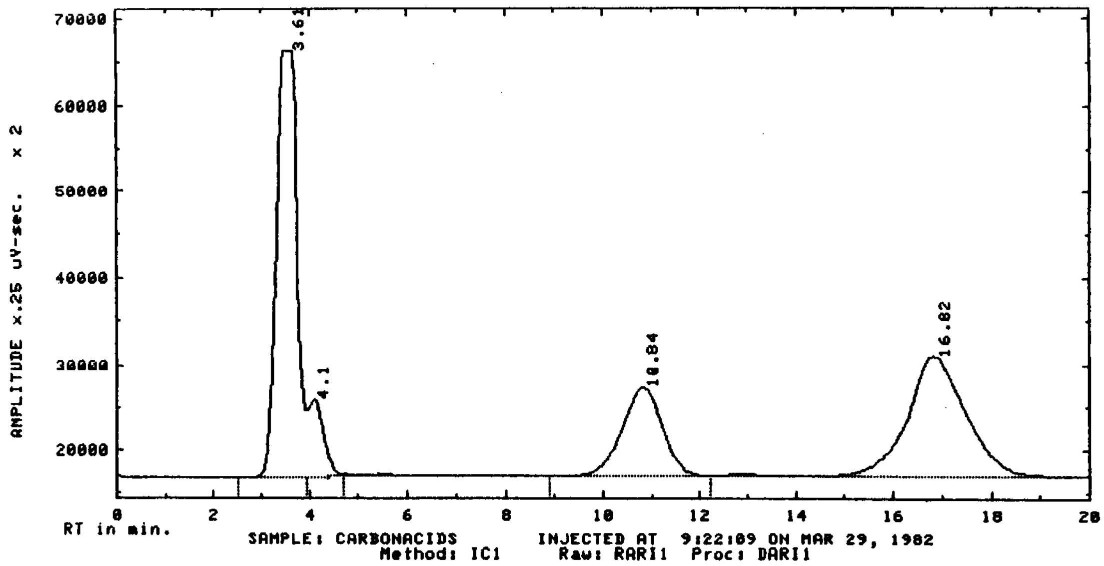


FIGURE 6 Determination of carboxylic acids in water.

References

1. D. Kasiske and M. Sonneborn, *Labor Praxis* **4,** 76 (1980).
2. Council of the European Communities, Richtlinie des Rates vom 15. Juli 1980 über die Qualität von Wasser für den menschlichen Gebrauch, *Amstblatt der Europäischen Geimeinschaften* **23,** 11 (1980).
3. W. Leithe, Umweltschutz aus der Sicht der Chemie, Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, 1975.
4. P. Obermann and G. Bundermann, *Wasser und Boden* **10,** 289 (1977).
5. T. Darimont and M. Sonneborn, Nitrat im Trinkwasser der Bundesrepublik Deutschland, Aktuelle Fragen der Umwelthygiene. Schriftenreihe des Vereins für Wasser-, Boden- und Lufthygiene (Gustav Fischer Verlag, Stuttgart, 1981) Vol. 52, pp. 187–195.
6. F. Selenka, Die Trinkwasserverordnung, Einführung und Erläuterung für Wasserversorgungsunternehmen und Überwachungsbehörden. (Erich Schmidt Verlag, Berlin, 1976), pp. 151–159.
7. G. Heide, W. Kley and H. Werner, *Zeitschrift der Deutschen Geologischen Gesellschaft* **128,** 349 (1977).
8. K. Aurand, M. Barowsky, T. Darimont, G. Milde and R. Oetting, *The Science of the Total Environment* **21,** 71 (1981).