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Note

Determination of EDTA in water by high-performance liquid chromatography

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Ethylenediaminetetraacetic acid (EDTA) is used in industry, in agriculture and in the home. In particular, it is used as a substitute for phosphates in detergents. It has not been shown to be toxic, but it is able to complex heavy metals. This property becomes a problem when EDTA after use is dissipated in the environment.

To determine the presence and quantity of EDTA a widely used method, also in our laboratory, is the gas chromatographic (GLC) one described by Rudling[1]. In this method EDTA is converted into its more volatile methyl ester and then measured by GLC. In practice, however, this method sometimes fails and peaks are not obtained. A reasoned explanation for such an absence could not be found, but probably the instability of the methyl ester or an irreversible adsorption in the column or syringe[2] is the cause.

A method therefore has been developed that is less susceptible to failures by making use of high-performance liquid chromatography (HPLC). It has the advantage that the sample can be directly injected after adding only one reagents. It is important, however, that the EDTA is in a stable form, *i.e.*, the iron(III)–EDTA complex. The time needed for an analysis is 7 min.

EXPERIMENTAL

HPLC system

The column used was an anion exchanger, Partisil 10 SAX (Whatman) (25 cm × 4.6 mm I.D.). To prevent pollution of the analytical column a guard column was used, packed with Vydac 301 SB (5 cm × 4.6 mm I.D.). A Varian 5020 liquid chromatograph and a Varichrom UV detector (258 nm, bandpath 8 nm) were employed. The data were handled with the Vista 401 system of Varian.

Eluent

The eluent was a solution of 30 g NaCl and 3 ml glacial acetic acid in 1 l of water (pH 3.1). It was passed over a 0.45-μm membrane filter before use.

Sample treatment

The samples first were passed over a 0.45-μm membrane filter to prevent clogging of the chromatographic system by solids from the sample. Then 50 μl of iron

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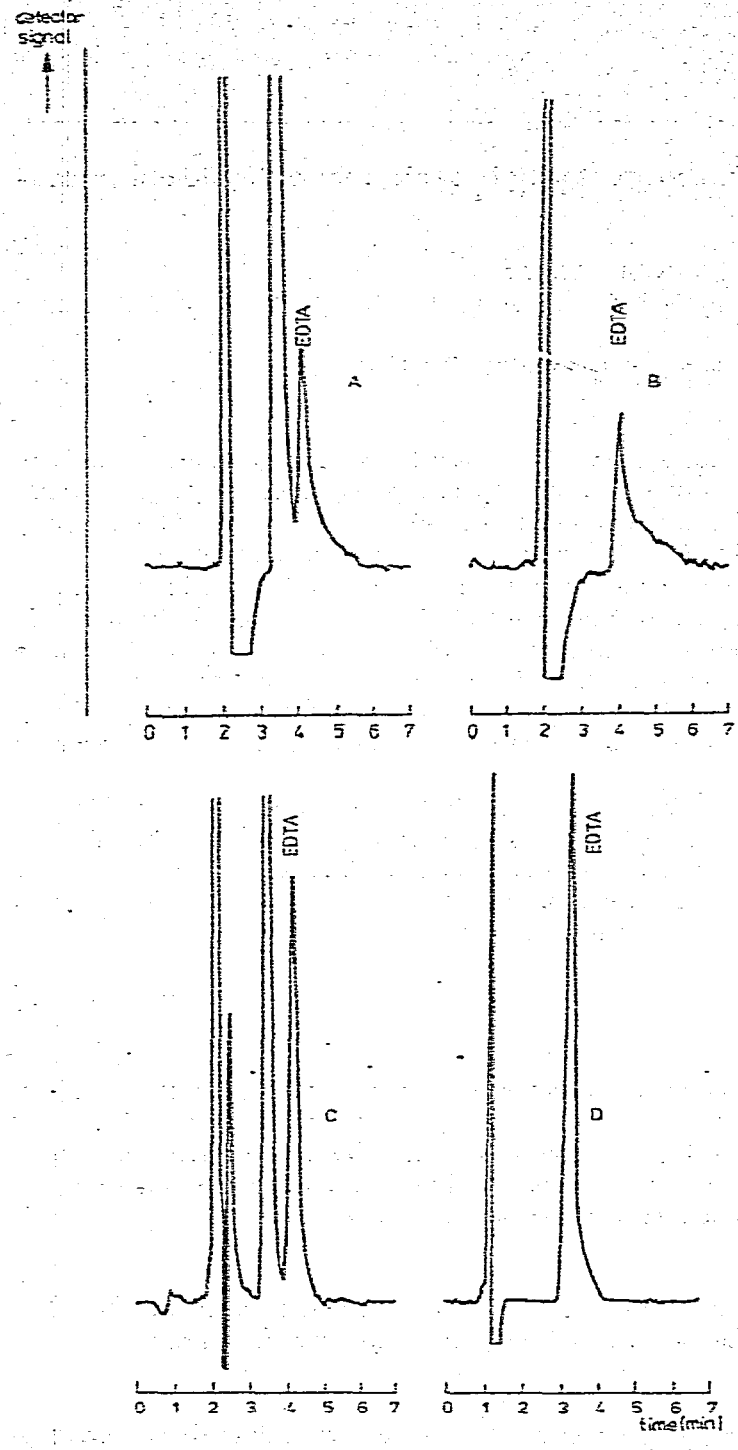

Fig. 1. Chromatographic analysis of EDTA. Column: 25 cm × 4.6 mm I.D. packed with Partisil 10 SAX. Guard column: 5 cm × 4.6 mm I.D. packed with Vydac 301 SB. Eluent: 30 g NaCl and 3 ml glacial acetic acid in 1 l of water, pH 3.1; flow-rate 1.5 ml min^{-1}. Detection: UV; attenuation 16. Samples (50 μl); A, water containing 5 mg l^{-1} EDTA without iron reagent, detection 220 nm; B, standard 5 mg l^{-1} without iron reagent, detection 220 nm; C, water containing 5 mg l^{-1} EDTA with iron reagent, detection 220 nm; D, water containing 5 mg l^{-1} EDTA with iron reagent, detection 258 nm.

reagent (4 g $FeCl_3$ and 30 ml glacial acetic acid in 100 ml water) were added to a 5-ml sample. If necessary, the sample was adjusted to a pH between 3 and 4 to prevent precipitation of the iron(III). This solution was injected via a 50-μl loop injector. As mentioned, the time of analysis was 7 min.

In order to prevent photochemical degradation of the EDTA in the presence of iron[2], the samples were stored in the dark until injection.

RESULTS AND DISCUSSION

In water EDTA occurs as an anion, the extent of dissociation of which depends on the acidity of the solution. Through this property it is possible to separate EDTA from other organic compounds in water with an anion-exchange column (Fig. 1).

In Fig. 1 the first and the negative peak (2–3 min) are caused by water in the sample. Water does not match the eluent and therefore gives peaks when passing the detector. The second peak is due to organic compounds in the solution. With more heavily polluted samples, more peaks of organic compounds are present in the range from 2 to 4 min. The third peak is EDTA. From Fig. 1A it can be seen that the separation is sufficient to analyze EDTA in water. The peak is strongly tailing, however, and especially with a standard solution containing EDTA only, this is not acceptable (Fig. 1B). The tailing can be explained by the different forms in which EDTA can be present in water and ultimately in the analytical column. If EDTA is present in calcium form and the column contains a small amount of adsorbed iron, the EDTA will form a complex with the iron because the iron–EDTA complex is more stable. This results in the retention of EDTA and a tailing peak.

It was expected that tailing would diminish when EDTA was present in a very stable form and not susceptible to change. Under the conditions prevailing in the column (pH 3.1), the iron(III)–EDTA complex is the most stable one[3]. When adding some iron(III) to the sample an EDTA peak with a much better shape was obtained (Fig. 1C) and the retention time also was much more reproducible, *i.e.*, ± 1 sec compared with ± 3 sec in the absence of iron.

Moreover, iron(III)–EDTA has an absorption maximum at a higher wavelength, namely 258 nm[4]. This is an advantage in that the absorption of the other organic compounds in the solution is very low in contrast to their absorption at 220 nm. In Fig. 1D the peak of the other organic compounds has disappeared. In heavy polluted waste water, peaks were to be seen in the region from 2 to 4 min, but the separation from EDTA was still sufficient.

The amount of iron(III) reagent is not critical. Amounts differing from 20 to 100 μl in 5 ml of sample did not influence the results.

Linearity of the method

The method is linear in the range 0–50 mg l^{-1} in which EDTA may occur in polluted water samples (Fig. 2). The detection limit is approximately 0.2 mg l^{-1}.

Interfering substances and recovery

Addition amounts of 1 and 10 mg l^{-1} of Cd(II), Cr(III), Cu(II), Pb(II) and Zn(II), 200 mg l^{-1} of Ca(II) and 50 mg l^{-1} of Mg(II) to a 10 mg l^{-1} EDTA standard did not change the results. However, Co(II) resulted in a smaller peak, while a second peak appeared after 25 sec. This peak is caused by a Co(II)–EDTA complex which is

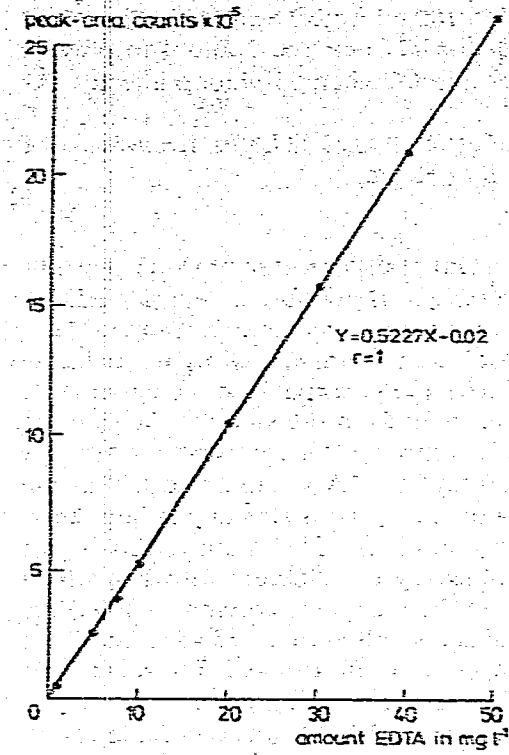

Fig. 2. Calibration curve of EDTA (peak-area counts *versus* amount of EDTA).

weaker than Fe(III)–EDTA, but probably forms an cobalt(III) complex which does not decompose in a reversible way. However, 10 mg l^{-1} Co(II) added to groundwater samples did not influence the results. The competition with other metal ions prevents the formation of Co(II)–EDTA. So, although Co(II) when present in groundwater generally, will not interfere, problems may arise when it is present in high amounts.

EDTA interacts with soil particles, as can be seen from the retardation of its transport through the soil[5,6]. When analyzing groundwater it is therefore important to filter the samples; then only the dissolved EDTA will be measured and not that adsorbed to suspended matter. To check the presence of interfering substances in filtered groundwater, recovery tests were carried out by adding various amounts of EDTA to water samples and determining the recovery (Table I). It may be concluded that, when low concentrations of EDTA are present, the recovery is good. Since additional peaks were not obtained in the chromatograms, interfering substances most likely were not present.

Comparison with the gas chromatographic method

In some groundwater samples the EDTA was determined by means of the above HPLC method, as well as by the GLC method of Rudling. The latter analyses were carried out by the laboratory of the Dutch Institute for Dairy Research (NIZO)[7].

TABLE I

RECOVERY OF EDTA IN GROUNDWATER SAMPLES

EDTA (mg l^{-1})			Recovery (%)
Present	*Added*	*Found*	
0	1.25	1.19	95
0	1.25	1.38	110
0.90	5	5.97	101
1.83	5	6.87	101
2.80	10	13.07	103
2.80	20	22.89	100
2.80	30	32.36	99

The results of the comparison are given in Fig. 3. It can be seen that the HPLC method systematically gives amounts 13% higher than the GLC method. This difference can be explained partly by the fact that the analyses were carried out in different laboratories, but also by the high amount of iron (approximately 10 mg l^{-1}) in the groundwater samples. Means *et al.*[8] reported that iron–EDTA and other EDTA chelates decreased the yield of the methyl ester of EDTA in the Rudling method. So in those cases the HPLC method will be more reliable than the GLC method.

Use of another eluent

The eluent described may be corrosive as chloride is present. For this reason

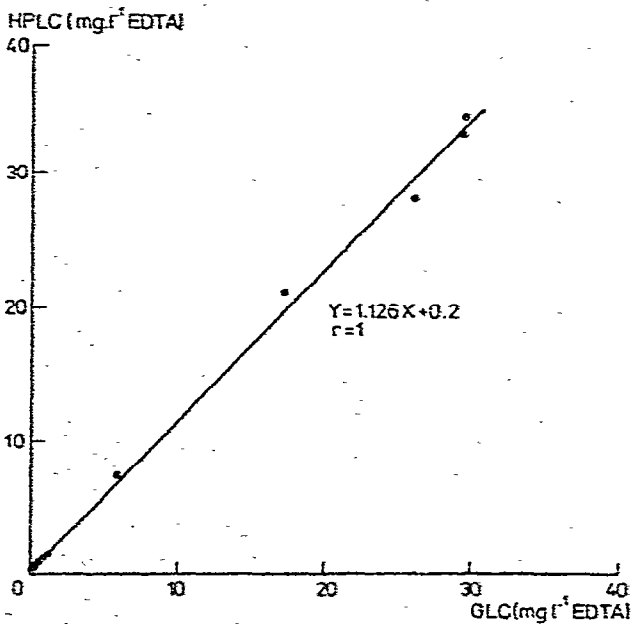

Fig. 3. Comparison of the results of the HPLC method and the GLC method of Rudling.

the instrument was always cleaned immediately after use by pumping distilled water through it. Corrosion problems were not encountered.

After concluding the experiments it was found that $NaNO_3$ instead of NaCl could be used. In the first experiments described nitrate could not have been used because it absorbs light at 220 nm. This does not occur at the wavelength (258 nm) used in the final experiments. An eluent containing 20 g $NaNO_3$ and 3 ml acetic acid in 1 l of water gave the same results as the eluent with NaCl.

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