

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
8 (2002)

**DETERMINATION OF EDTA AND NTA IN WATER
BY GAS CHROMATOGRAPHY**

Karel KOMÁREK^{a1}, Lucie GRYNOVÁ^a, Jiří MEDEK^b, Petr DOLENEK^b
and Martin FERENČÍK^b

^aDepartment of Analytical Chemistry, The University of Pardubice,
CZ-532 10 Pardubice

^bPovodí Labe, a.s., CZ-530 00 Hradec Králové

Received September 30, 2002

A simple method for the determination of nitrilotriacetic acid (NTA) and ethylene-diaminetetraacetic acid (EDTA) beside other aminopolycarboxylic acids in surface water and waste water by gas chromatography is described. First, water samples were dried by evaporating. The free acids were esterified by the mixture of n-butyl alcohol and acetyl chloride. The prepared n-butyl esters were identified by the capillary GC-MS and then determined by the capillary GC-FID. n-Butyl esters of aminopolycarboxylic acids NTA, EDTA, CDTA and DTPA were characterized by retention times under the chosen conditions.

¹ To whom correspondence should be addressed.

Introduction

Builders are very important components of detergents. The most used ones are zeolites, phosphates, nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). After using, these components contaminate surface water. To minimize the impact of washing powders on the environment, the Ministry of Environment and Czech Association of Soap, Washing and Cleaning Products Producers made an agreement, which defined the limit value of NTA and EDTA in products [1]. These acids and their salts are used also in pulp and paper industry, leather manufacture, in electroplating, textile or photographic materials treatment and so on. Nowadays, the Ca complex of EDTA is registered as a food additive. That is why the content of the acids and similar compounds starts to attract attention of ecologists and toxicologists.

Other aminopolycarboxylic acids used in a technical practice are diethylenetriaminepentaacetic acid (DTPA), cyklohexylenedinitrotetraacetic acid (CDTA), methylglycine-diacetic acid (MGDA), β -alaninediacetic acid (ADA), 1,3-propylenediaminetetraacetic acid (PDTA), *N,N*-di-(hydroxyethyl)glycine (DHEG), hydroxyethylenediaminetetraacetic acid (HEDTA), *N*-(2-hydroxyethyl)-iminediacetic acid (HEIDA). Furthermore, the other compounds seem to be used in future, e.g. aminotrimethylenephosphoric acid (ATMP) and *N,N,N',N'*-tetrakis(1-hydroxy-isopropyl) ethylene diamine (Quadrol).

The Ways of Analysis of EDTA and NTA

Generally, the first step of analysis by the gas chromatography is a concentration procedure of a sample such as application of the ion exchange column after foregoing pH treatment by formic acid. The eluate from the columns is dried by evaporation and then a derivatization is carried out. The obtained derivatives are extracted from the reaction mixtures by the suitable solvent. The combined extracts are dried with anhydrous sodium sulphate and sometimes they can be concentrated by evaporating. Then they are injected into the gas chromatograph. Compounds such as DTPA, CDTA and the others are used as the internal standards for the determination. Both acids are transformed into *n*-butyl esters [2,3], *n*-propyl esters [4], isopropyl esters [5], methyl esters [6] and trimethylsilyl esters [7]. The derivatives are analyzed either on packed columns [3,7–9], or on capillary columns [2,5,6].

The determination of EDTA and NTA in water can be carried out by liquid chromatography [8,10], polarography, colorimetry [8], micellar electrokinetic capillary chromatography [11], anion-exchange chromatography and inductively coupled plasma mass spectrometry (ICP-MS) [12] and LC-MS [13].

We tried to find out an inexpensive but suitable method of determination of

EDTA and NTA next to CDTA and DTPA in surface water and in waste water by gas chromatography.

Experimental

Chemicals

EDTA, NTA, CDTA, DTPA, *n*-butanol for GC analysis, *n*-hexane for organic analysis and isopropyl alcohol for synthesis were purchased from Merck, stearonitrile from Aldrich, hydrochloric acid 35 % p.a. and sodium hydroxide p.a. from Lachema and sodium sulphate from Litolab.

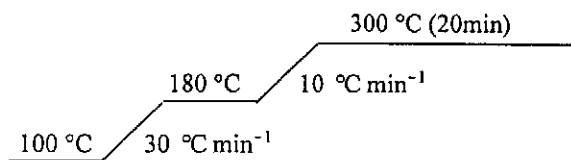
Instrumentation

Gas chromatograph GC 8000, detector FID, integrator DP 700 from Carlo Erba, Fisons Instrument, Italy and capillary column HP 5, 18m × 0.32mm × 0.25 mm from HP, USA were used.

GC Analysis

Injection: splitless 1ml, temperature of injection: 290 °C, temperature of detector: 300 °C.

Temperature gradient of column:



Esterification Agent

The esterification agent was prepared by mixing 90ml *n*-butanol and 10ml acetyl chloride. This agent could be used for a month.

Sample Preparation

Solutions were prepared from 101.5 mg NTA, 99.8 mg EDTA, 100.2 mg CDTA and 99.3 mg DTPA. These weighed quantities were dissolved in 100ml water. Then 2 ml sodium hydroxide (1 mg l^{-1}) was added. From these solutions, calibration curves were constructed.

Internal Standard

Stearonitrile was used as an internal standard. This solution was prepared by diluting 100.3 mg stearonitrile with 5 ml *n*-heptane.

Water Samples

Water samples were stored with 10 ml formaldehyde in the refrigerator.

Derivatization

The water sample was evaporated from a volume of 100 ml to 10 ml. This solution was quantitative transferred into a 10 ml vial and evaporated until dry in a thermostat. Then 10 ml hydrochloric acid (1 mol l^{-1}) was added. The solution was evaporated until dry. Then 2 ml esterification agent were added and the solution was heated 30 minute at $90 \text{ }^\circ\text{C}$. After cooling to room temperature, 2 ml *n*-hexane and 2 ml internal standard solution were added. The solution was transferred into a 50 ml volumetric flask containing 1 ml sodium hydroxide (1 mol l^{-1}). The flask was made up to the mark with water and then shaken for one minute. The hexane layer was isolated and dried by sodium sulphate. The solution was evaporated to 100 μl . This concentrate was stored in a 1 ml vial in the refrigerator.

Results and Discussion

The retention times of NTA, EDTA, CDTA and DTPA were measured (see the conditions in Experimental). These retention times are given in Table I. They are arithmetic averages from six measurements. Figure 1 shows the chromatogram of separation of acids after their derivatization. The content of these acids was determined by using the internal standard.

The water samples were sampled from the river Elbe in January, February and March 2001. The results of determination of NTA, EDTA and CDTA are

given in Table II. Figure 2 shows the chromatogram of water sample taken in Obříství on 28.2.2001.

Table I Average retention times (t_R) and standard deviation for aminopolycarboxylic acids

	Aminopolycarboxylic			
	NTA	EDTA	CDTA	DTPA
t_R (min)	10.13	16.14	19.93	30.77
SM	0.05	0.04	0.09	0.03

Table II Results of determination of NTA, EDTA and CDTA in river samples and samples from waste water treatment plants

Place and date of sampling	NTA, $\mu\text{g l}^{-1}$	EDTA, $\mu\text{g l}^{-1}$	CDTA, $\mu\text{g l}^{-1}$
Lysá n. Labem, 31.1.2001	1.96	3.85	
Děčín, 31.1.2001	2.7	5.94	
Obříství, 28.2.2001	9.23	9.82	5.79
Valy, 28.2.2001		3.92	
Hřensko right riverside, 28.2.2001	14.78	12.68	
Hřensko left riverside, 28.2.2001	7.78	10.78	6.48
Valy, 28.3.2001		6.19	
Lysá n. Labem, 28.3.2001	2.51	7.923	
Děčín, 28.3.2001	2.94	5.46	
Hřensko right riverside, 28.3.2001		3.24	
Hřensko left riverside, 28.3.2001		3.70	
Waste water treatment plant Vamberk, 28.3.2001		14.65	
Waste water treatment plant Mezísvětí, 28.3.2001		10.60	

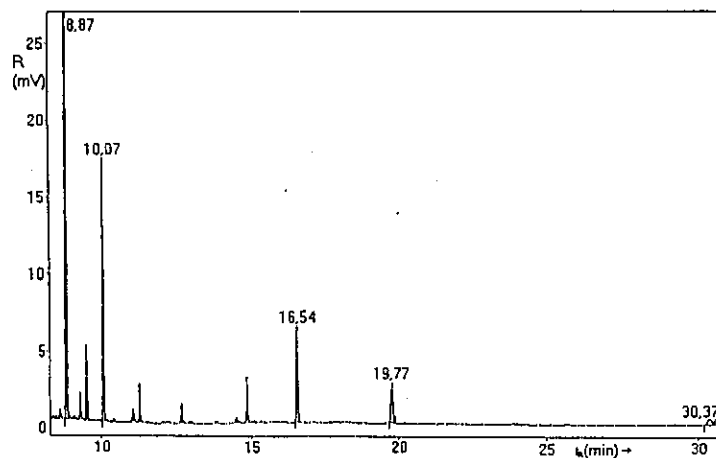


Fig. 1 Chromatogram of the model mixture of NTA, EDTA, CDTA and DTPA after their derivatization into *n*-butyl esters: Retention times: Stearonitrile (internal standard): 8.87 min, derivatives of acids NTA 10.07 min, EDTA 16.54 min, CDTA 19.82 min, DTPA 30.37 min. Fused silica capillary column HP5, 18 m × 0.32 mm × 0.25 μm, programmed temperature: 100 °C → 180 °C, 30 °C min⁻¹, 180 °C → 300 °C (20 min), 10 °C min⁻¹. Carrier gas: helium, injection: spiltless, 1 μl

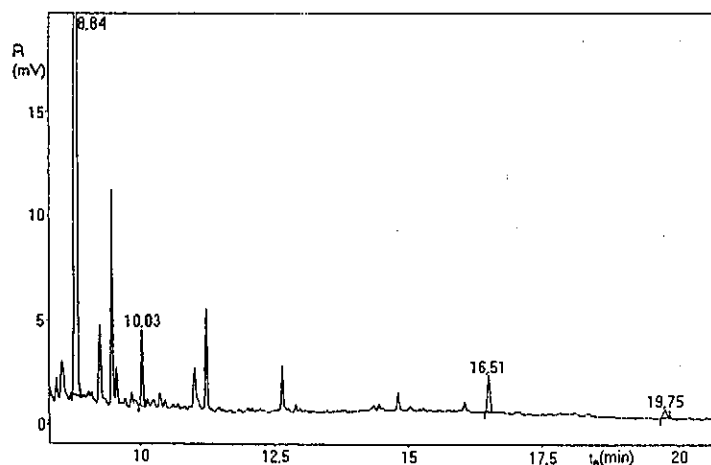


Fig. 2 Chromatogram from determination of NTA, EDTA and CDTA as *n*-butyl esters in the river Elbe water sample. Sampling was carried out in Obfiství on 28th February 2001. Retention times: stearonitrile (internal standard) 8.84 min, derivated acids NTA 10.03 min, EDTA 16.51 min, CDTA 19.75 min. The column and working conditions were the same as in the case of Fig. 1

Conclusion

We succeeded in finding out a simple and inexpensive method of determination of NTA and EDTA in surface and waste water by gas chromatography. Concentration and derivatization of the compounds were carried out before the GC analysis. The method can be used also for the determination of other aminopolycarboxylic acids. The preliminary experiments indicate the possibility of application of more sensible selective detectors, such as NP and MS.

References

- [1] Pitter P.: XXXIV. *Seminar on Tensides and Detergents*, Proceedings of lectures, p. 32, Bojnice, 2000, Slovak Republik.
- [2] Schaffner C., Giger W.: *J. Chromatogr.* **312**, 413 (1984).
- [3] Williams D.T., Benoit F., Muzika K., Grady R.O.: *J. Chromatogr.* **136**, 423 (1977).
- [4] Lee H.B., Peart T.E., Kaiser K.L.E.: *J. Chromatogr. A* **738**, 91 (1996).
- [5] Randt C., Wittlinger R., Merz W.: *Fresenius J. Anal. Chem.* **346**, 778 (1993).
- [6] Nishihawa Y., Okumura T.: *J. Chromatogr. A* **690**, 109 (1995).
- [7] Subach D.J., James J.E.: *J. HRCCC* **309**, 1016 (1980).
- [8] Kirk P.W., Perry R., Lester J.N.: *Intern. J. Environ. Anal. Chem.* **12**, 293 (1982).
- [9] Games L.M., Staubach J.A., Kappeler T.U.: *Tenside Deterg.* **18**, 262 (1981).
- [10] Longman G.F., Stiff M.J., Gardiner D.K.: *Water Res.* **5**, 1171 (1971).
- [11] Harvey S.D.: *J. Chromatogr. A* **736**, 333 (1996).
- [12] Amman A.A.: *J. Chromatogr. A* **947**, 205 (2002).
- [13] Reemtsma T.: *TrAc Trends in Analytical Chemistry* **20**, 500 (2001).