Journal of Chromatography, 190 (1980) 188–192

CHROM. 12,541

Note

Determination of multifunctional carboxylic acids in the presence of iron by gas chromatography

R. M. CASSIDY, R. HARPUR and S. ELCHUK

General Chemistry Branch, Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories, Chalk River, Ontario K0J 1J0 (Canada)

(First received July 11th, 1979; revised manuscript received September 27th, 1979)

Multifunctional carboxylic acids such as oxalic acid, citric acid and ethylenediaminetetraacetic acid (EDTA), are often used in nuclear decontamination procedures. In addition, complexing agents such as EDTA, which biodegrades slowly, may be important in the mobilization of subsurface radioactive wastes[1]. Accurate analytical procedures are a prerequisite for an understanding and modelling of decontamination processes and the terrestrial migration of radionuclides.

The determination of carboxylic acids by gas chromatography (GC) is an area that has received considerable attention. Formation of alkyl esters is commonly used to improve the GC separation of carboxylic acids and this subject has been reviewed in a recent monograph[2]. There is voluminous literature on the GC determination of oxalic and citric acids and several reports have described the determination of aminocarboxylic acids such as EDTA[3–6]. Our investigation of these or similar techniques gave poor repeatabilities for EDTA, especially for small samples (1 μl), and more importantly, in the presence of iron, repeatabilities for all three acids became worse and sample recoveries were low. The interference from iron is particularly important since large concentrations of iron can be present in radioactive waste solutions, and depending on the redox conditions existing at a particular point in an aquifer[7], significant concentrations of iron (several μg/ml) can be found in groundwater. This report summarizes the results of an investigation of the GC separation and determination of oxalic and citric acids, and EDTA, in the presence of large concentrations (10–300 μg/ml) of iron.

EXPERIMENTAL

Reagents

The esterification reagents studied were: 14% BF_3 in methanol and 12% BCl_3 in methanol (Chromatographic Specialties, Brockville, Canada), Meth Elute (0.2mol/l trimethylanilinium hydroxide in methanol, Chromatographic Specialties), and Methyl-8 (dimethylformamide dimethylacetal, Chromatographic Specialties).

Chromatography

Sample components were separated on glass columns (1.8 m × 3.2 mm I.D.)

which were programmed from 65 to 250° at 8°/min for 10% Silar 9CP (cyanosilicone) on Chromosorb W AW (Chromatographic Specialties) and from 50 to 285° at 8°/min for 3% OV-17 (silicone) on Chromosorb W HP (Chromatographic Specialties). Eluites were detected with a flame ionization detector.

Standard and sample analyses

Standards and samples containing iron were placed in opaque containers and stored in the dark. Prior to the addition of the derivatizing reagent, all samples were treated as quickly as possible to minimize exposure to light. The following procedure is similar to that reported previously[2].

The pH of the sample was adjusted (usually 4.5–7) with lithium hydroxide and a sample aliquot was added to a 5-ml vial. The sample was dried at 125° and on cooling, 1 ml of 14% BF_3 in methanol was added. The vial was sealed with a PTFE–silicone septum and heated at 100° for 30 min. After cooling, 0.5 ml of chloroform and 3 ml of a buffer (phosphate, 1 mol/l, pH 7) were added and the mixture was agitated for ≈ 1 min. A 1-μl aliquot of the chloroform layer was injected into the gas chromatograph; the syringe needle was held in the injection port until the solvent peak appeared on the chromatogram (≈ 15 sec).

RESULTS AND DISCUSSION

Derivatization

Adjustment of the sample pH increased the solubility of some of the acids in the derivatizing solution and also prevented losses of lower-molecular-weight acids during the drying step. Oxalic acid, citric acid and EDTA did not react with Methyl-8 but did so slowly with MethElute. With prolonged (≈ 14 h) heating at 100° the reaction of the free acids with MethElute was quantitative but no reaction was observed with the alkali metal salts. Small amounts of water (0.05 ml in 1 ml of reagent) had no effect on the derivatization. Both BCl_3 and BF_3 reagents gave quantitative recoveries; the remainder of this discussion will refer to only the BF_3 reagent.

Chromatography

The chromatography on both OV-17 and Silar 9CP was satisfactory but the less polar OV-17 did not separate the more volatile esters from the solvent peak. Consequently, Silar 9CP was used for the majority of this work; a representative chromatogram is shown in Fig. 1.

During these studies poor repeatabilities and recoveries (both peak height and peak areas) were observed for EDTA esters. Table I shows that the repeatability for EDTA improved to an acceptable level if the syringe needle was held in the injection port after sample injection. This procedure had no effect on the good recoveries and repeatabilities observed for citric and oxalic esters and the ratio of citric ester response to EDTA ester response (see Table I) was a good measure of EDTA recovery. It appears that the EDTA ester can be adsorbed onto the metal surface of the syringe needle, possibly as a result of the availability of two nitrogen donor atoms in the EDTA ester, and has to be desorbed by providing a longer "injection time".

Both the OV-17 and Silar 9CP columns showed some irreversible adsorption of EDTA esters for new columns or when the columns were held at high temperatures

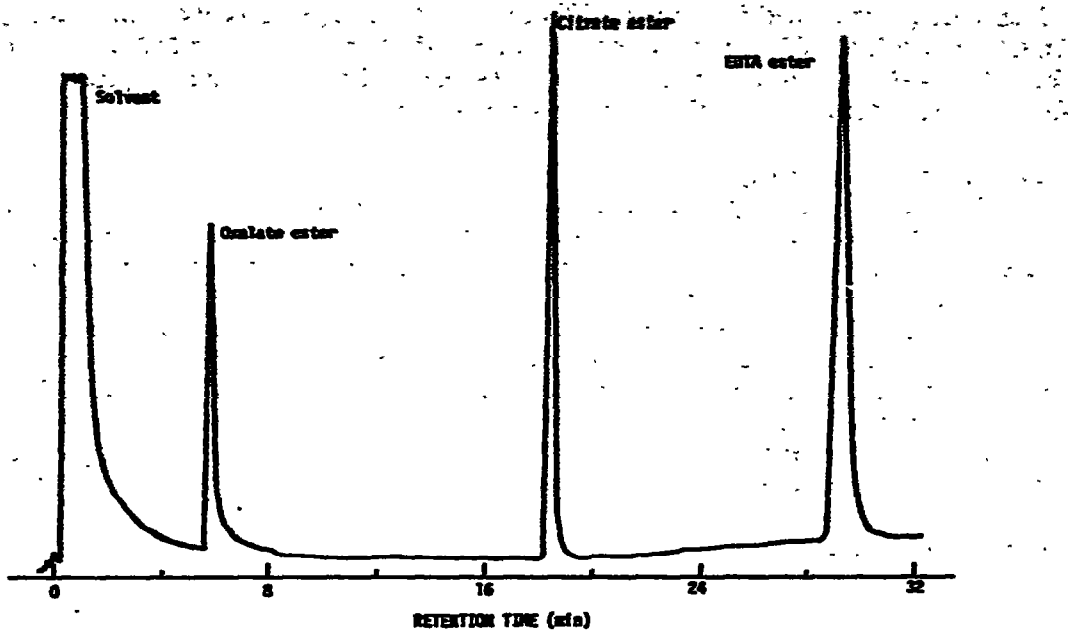

Fig. 1. Separation of methyl esters of oxalic, citric and EDTA. The concentration of each acid in the original sample was $\approx 2 \cdot 10^{-3}$ mol/l; flame ionization detector set at 10^{-2} of maximum sensitivity.

TABLE I

EFFECT OF SAMPLING TECHNIQUE ON REPEATABILITY

Sample (1 µl)	*Injection* time (sec)*	*Peak height (mm)*				
		1	*2*	*3*	*4*	*5*
Citric	9	562	570	560	570	574
Oxalate	9	169	168	163	169	172
EDTA	9	280	263	313	320	317
EDTA	15	103	104	111	110	111
		Peak area ratio				
Citric: EDTA	≈3	0.96	0.63	1.15	1.02	0.98
Citric: EDTA	15	0.66	0.65	0.64	0.65	0.64

* Injection time is the time that the syringe needle remains in the injection port; the bulk of the sample is rapidly introduced into the injection port.

for an extended period. Losses were generally small (5–10%) and this problem can be eliminated if 5–10 µg of EDTA ester are injected at the start of each working day. An on-column silylating reagent, Silyl-8, was also used but this did not prevent the irreversible adsorption.

Fig. 2 shows that calibration curves are linear with respect to peak area but not with respect to peak height; this was also observed for a series of aqueous standards, dilutions of a derivatized standard, and a set of citric standards in the concentration range of 10–100 µg/ml. Smaller acid concentrations can be determined with

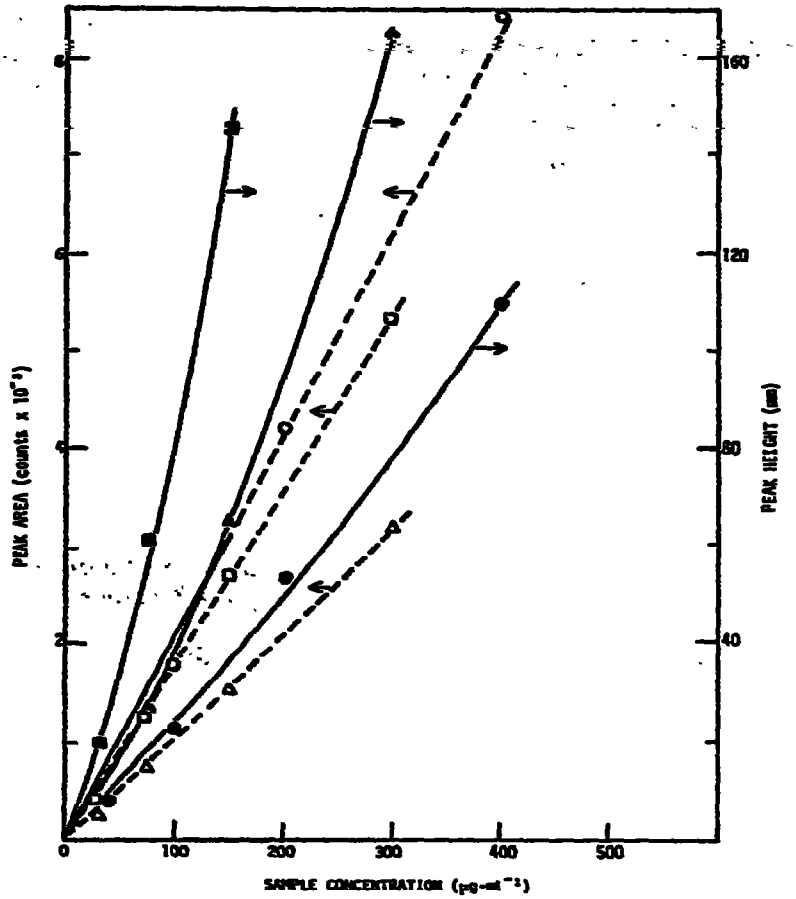

Fig. 2. Standard curve in terms of peak area and peak height. ●, EDTA; ■, citric acid; ▲, oxalic acid. – – – –, Peak area against concentration; ——, peak height against concentration.

appropriate changes in the volumes of reagents used and, for higher-molecular-weight acids, by evaporation of the chloroform extract (ref. 3 and this work).

Effect of iron

Irreproducible and low results, particularly for EDTA, were obtained when the samples contained 10–300 μg/ml of Fe(II) or Fe(III). Losses of ≈ 10% were often observed for EDTA in the presence of iron after <24 h; standards containing Cu(II) (90 μg/ml) did not exhibit similar losses. Solutions would slowly turn a dark yellow color, the pH of the solution would rise, and eventually a precipitate (ferric hydroxide) would appear. The rate at which these changes occurred varied directly with the exposure of the sample to both light and air but showed little dependence on the iron concentration, within the range studied (10–300 μg/ml).

Time studies (Table II) indicated that decomposition increases in the order EDTA < oxalic < citric. For a mixture of the three acids, the decomposition followed the order of the conditional stability constants of the iron complexes: citric≈

TABLE II

DECOMPOSITION OF ACIDS IN THE PRESENCE OF IRON

The concentration of the acids and iron was $\approx 2 \cdot 10^{-3}$ mol/l.

Time (h)	*% Decomposition of individual solutions*		
	Citric	*Oxalic*	*EDTA*
0	0	0	0
72	47	14	6
144	53	22	9
192	60	25	10
312	77	46	28
	% Decomposition of mixture		
0	0	0	0
144	0	5	11
192	1	10	30
312	60	30	76

oxalic < EDTA. The decomposition rates shown in Table II increased when contact with both air and light was maintained. Samples stored in the dark showed no decomposition after 312 h.

The decomposition of these acids appears to occur by a cyclic photoreduction/air oxidation of their iron complexes. In 1952 Jones and Long[8] described such a process for the complex $FeEDTA^-$.

$$FeEDTA^- \xrightarrow{h\nu} FeEDTA^{-*}$$

$$FeEDTA^{-*} \longrightarrow FeEDTA^{2-} + \text{EDTA decomposition products}$$

$$4\,FeEDTA^{2-} + 2\,H_2O + O_2 \longrightarrow 4\,FeEDTA^- + 4\,OH^-$$

These authors reported a partial decomposition of EDTA but this was not observed by Hill-Cottingham[9]. The present results show that this decomposition does occur and that it can introduce a large negative analytical error. This type of decomposition may be general for carboxylate ligands and thus could affect a wide variety of analytical procedures.

REFERENCES

1 J. L. Means, D. A. Crerar and J. O. Duguid, *Science*, 20 (1978) 1477.
2 A. Darbre, in K. Blau and G. Kind (Editors), *Handbook of Derivatives for Chromatography*, Heyden & Son, Philadelphia, Pa., 1978, Ch. 2, p. 39.
3 L. Rudling, *Water Res.*, 5 (1971) 831; 6 (1972) 871.
4 Y. K. Chau and M. E. Fox, *J. Chromatogr. Sci.*, 9 (1971) 271.
5 M. Mihara, R. Amand, T. Kondo and H. Tanabe, *Shokuhin Eiseigaku Zasshi*, 11 (1970) 88; *C. A.*, 73 (1970) 97446t.
6 D. T. Williams, *J. Ass. Off. Anal. Chem.*, 57 (1974) 1383.
7 D. R. Champ, J. Gulens and R. E. Jackson, *Can. J. Earth Sci.*, 16 (1979) 12.
8 S. S. Jones and F. A. Long, *J. Phys. Chem.*, 56 (1952) 25.
9 D. G. Hill-Cottingham, *Nature (London)*, 175 (1955) 347.