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Journal of Chromatography A, 690 (1995) 237–242

JOURNAL OF CHROMATOGRAPHY A

Short communication

Calibration and determination of volatile fatty acids in waste leachates by gas chromatography

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First received 1 August 1994; revised manuscript received 19 October 1994; accepted 3 November 1994

Abstract

Low-level radioactive waste leachates were analyzed for volatile fatty acids by gas chromatography as part of the continuing waste management program at the Chalk River Laboratories. An existing method was optimized whereby carboxylic acids were detected at the mg/l level with a precision of 5% or better for C_2–C_7 acids and an accuracy of 3% or better for acetic acid. Parameters such as sample handling, calibration and accuracy are discussed.

1. Introduction

Low-level radioactive wastes (LLRWs) contain large amounts of cellulose-based materials such as paper towels, used clothing, corrugated board, etc. After waste burial, disposal, or in leachates, microbial degradation of the organic substrate produces high quantities of dissolved organic matter (DOM) [1–4]. Volatile fatty acids (VFAs), defined here as C_2–C_7 monocarboxylic aliphatic acids, were the most abundant class of compounds in the DOM present in landfills or LLRW leachates [1,5–7]. VFAs, particularly acetic acid, may have an impact on Pu migration in soils [8] thus monitoring its contents and production with time in the leachates could be important. An experimental program was carried out at the Chalk River Laboratories (CRL) to monitor the decomposition products of LLRWs. Wastes were collected and compacted into bales, and eight such bales were leached with water in a closed-loop recirculation system [1].

The VFA content in the leachates was determined by liquid–liquid extraction of the aqueous phase with ether, and a 10-μl aliquot of the organic phase injected in a GC system equipped with flame ionization detection (FID) [9–12]. In this method, since the VFAs have to transfer from the aqueous to the organic phase, the reproducibility and calibration could represent a problem, especially if the extraction is not quantitative. The original method [9,11] did not include a calibration procedure, so we had to develop a calibration method for this work. We have used a commercial mixture of C_2–C_7 carboxylic acids, which were liquid–liquid extracted similarly to the leachate samples. However, when the slope of the individual calibration curve of each VFA was plotted as a function of the number of carbon atoms, the signal did not increase linearly as it should [13] for acetic and propionic acids. We suspected that this was due

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SSDI 0021-9673(94)01081-1

to a non-quantitative extraction of acetic acid. We have also used a total carbon analyzer as an independent method to check for dissolved organic carbon content in the standards. Our work aims to verify the accuracy of the calibration procedure for the preparative work and analysis of the samples, and to improve our precision. Potential problems associated with calibration will be briefly discussed.

2. Experimental

2.1. Instruments

A Perkin-Elmer Model 8500 GC–FID system was used with a stainless-steel column (6 ft. × 0.085 in. I.D.; 1.83 m × 0.216 cm I.D.) packed with GP-10% SP-1200/1% H_3PO_4 on 80–100 mesh Chromosorb W AW (Supelco, Bellefonte, CA, USA). The carrier gas was helium (Linde, high purity) at a flow-rate of 30 ml/min. The detector base and injection port temperatures were set at 250°C. The runs were performed using a temperature program consisting of a 3-min isothermal period at 70°C, followed by a 10°C/min temperature ramp to 130°C, a second temperature ramp (5°C/min) to 180°C, and a 1-min isothermal period at 180°C. The stainless-steel column used may not represent an adsorption or ghosting problem as the amounts of VFAs are high [1] and this combination of gas flow-rate and temperature programming gives a good separation (Fig. 1).

The total carbon analyzer used for the calibration was a Dohrmann DC-80 (Rosemount Analytical, Santa Clara, CA, USA). The instrument was calibrated in the 400 mg C/l range with potassium hydrogen phthalate. The VFA content of the standards agreed within 2% with this instrument for up to 500 mg C/l. Above this level, dilution was necessary.

2.2. Sample preparation

The leachate samples were acidified at pH 2 using concentrated nitric acid for dissolved metal analysis for a separate study. An aliquot of this

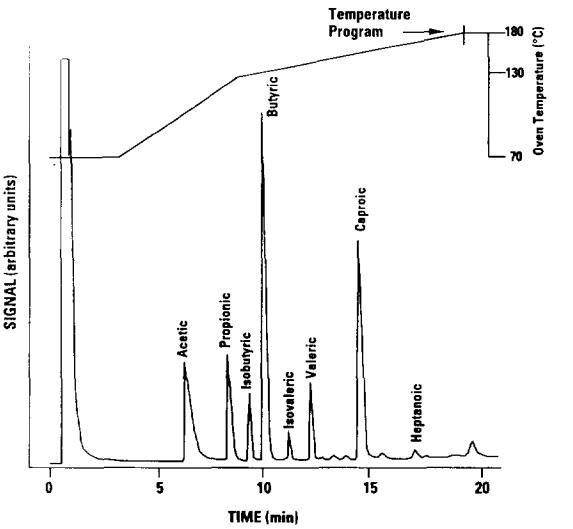

Fig. 1. Chromatogram of VFA extract from a waste leachate sample, also showing the GC temperature program.

solution was taken for VFA analysis. This change in acid (sulfuric acid was used in the original procedure [9]) did not change the accuracy (results not shown). A 1-ml aliquot of the acidified leachate was shaken along with 1 ml of diethyl ether for approximately 30 s. The supernatant ether phase was quantitatively transferred to a volumetric flask using a Pasteur pipette. The volume of ether extract was adjusted to the 1-ml mark and a small amount (approximately 0.2 g) of anhydrous magnesium sulfate was added to absorb traces of water. The extract was allowed to stand for approximately 10 min in an ice bath and it was then transferred to a 1-ml reaction vial with a Mininert cap. A 10-μl volume of this extract was injected into the GC system using a syringe. The extracts could be stored at room temperature in these vials for up to a week.

2.3. GC calibration and VFA standards

A series of standards for the calibration curves was prepared in the same manner as described above. Individual calibration curves were obtained for each compound using the standard VFA mixture, in concentrations ranging from 0 to 10 mM for all VFAs except for acetic acid (0

to 100 mM). The standards used for the successive extractions were prepared using dilute acetic acid (calibrated with the carbon analyzer) mixed in equal proportions with the primary VFA standard to obtain a final concentration of 0.057 M for acetic acid and 0.005 M for the other VFAs.

2.4. Chemicals

The primary C_2–C_7 VFA standard mixture was purchased from Matreya (Pleasant Gap, PA, USA; catalog No. 1075). These other chemicals were used: anhydrous diethyl ether (Fisher; 99 + % purity), anhydrous magnesium sulfate (Fisher, 98.0%) and potassium hydrogen phthalate dried overnight at 60°C (Fisher, 99.95–100.5%, ACS primary standard).

3. Results and discussion

Fig. 1 shows a chromatogram from the analysis of an actual leachate sample. The 3-min isothermal period allowed for the complete elution of ether, so the signal reached the baseline prior to elution of acetic acid. A gradual temperature gradient was used after 9 min to ensure a good separation of the heavier VFAs. Table 1 shows the precision for three separate extractions. In general, our experiments have shown that there was a larger variability between duplicate extractions than between duplicate injections of the same organic aliquot. We have consistently obtained a precision of 5% or better in separate extractions.

The leachate samples and calibration standards (C_2–C_7 VFAs) were liquid–liquid extracted under the same conditions after pH adjustment to <2 to ensure protonation of the carboxylic acid groups. Despite the caution used to perform the extractions, the slopes of the calibration curves did not increase proportionally with the number of carbon atoms for all the VFAs (□, Fig. 2). This lead us to examine the extraction step in detail.

Theoretical considerations (Tables 2 and 3) suggested that quantitative transfer was possible for the more hydrophobic VFAs, but not for acetic and propionic acids. The data in Tables 2 and 3 use the capacity of a substrate to transfer to the organic phase, given by:

$$k' = P \cdot \frac{V_o}{V_a}$$

where k' = capacity factor, P = liquid–liquid partition coefficient, V = volume of solution, and the subscripts o and a stand for organic and aqueous phases, respectively. P is defined as [14]:

Table 1
Results showing the precision of triplicate extracts from a leachate sample

Acid	Peak area for injection No: (arbitrary units)			Average	R.S.D. (%)[a]
	1	2	3		
Acetic	1599	1657	1706	1654	2.7
Propionic	913	930	950	931	1.6
Isobutyric	446	452	455	451	0.9
Butyric	2643	2665	2701	2667	1.0
Isovaleric	167	169	171	169	0.9
Valeric	652	654	664	657	0.8
Caproic	2060	2060	2107	2071	1.2
Heptanoic	56.9	53.3	60.5	56.9	5.2

[a] R.S.D. = Relative standard deviation = 100 · standard deviation / mean.

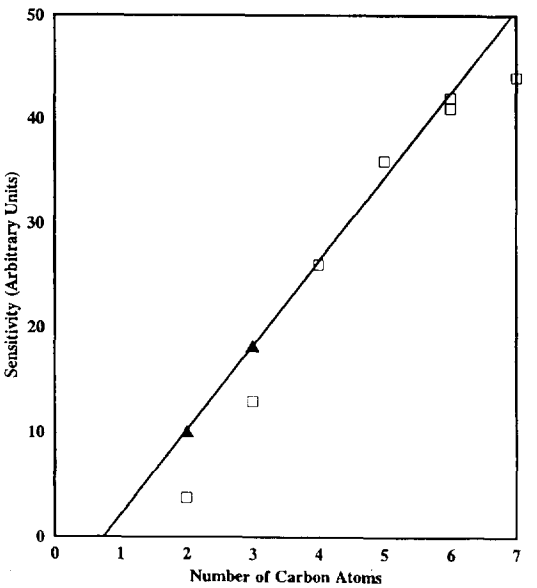

Fig. 2. Sensitivity (or response factor) of the individual VFAs as a function of the number of carbon atoms of the compounds. Note that the line does not go through the origin, since the FID signal is weak for oxygenated carbon compounds such as carboxylates [13]. □ = Experimental; ▲ = corrected sensitivity; line = fitted C_2–C_6.

$$P = \frac{[\mathrm{VFA}]_o}{[\mathrm{VFA}]_a}$$

where the brackets [] denote concentrations. Table 2 shows that there is a linear relationship between the number of carbon atoms of the VFA and log P. The branched VFAs (isobutyric acid, etc.) are included in the relationship for chloroform, thus the C_2–C_6 relationship including the branched VFAs should also be linear for ether.

We consider a liquid–liquid extraction quantitative if 95% or more of the analyte is extracted into the organic phase, which translates to a log $k' \geq 1.25$ or log $P \geq 1.25$ for a 1 ml to 1 ml extraction. Note that in the Supelco method [11], a 1:2 organic-to-aqueous ratio was used, where theoretically only the C_6 or higher VFAs could transfer quantitatively. We have performed three successive extractions of the same aqueous standard, each time with a fresh ether layer to determine if the liquid–liquid extractions were quantitative with the C_2–C_7 VFAs (Table 4). Note that the individual VFA values (determined separately with the GC method) agreed within 3–11% of the label-declared value, and the sum of all the VFAs combined was within 1% of the total DOM value given by the carbon analyzer. In a separate run, the carbon analyzer values for acetic acid agreed within 3% with the GC method.

Table 3
Calculated log P for monocarboxylic aliphatic acids using the relationship of Table 2

Acid	No. of carbon atoms	Log P	
		From [14]	This work, calculated
Acetic	2	−0.34	−0.38
Propionic	3	0.2	0.18
Isobutyric	4		0.75
Butyric	4	0.68	0.75
Isovaleric	5		1.31
Valeric	5	1.24	1.31
Isocaproic	6		1.87
Caproic	6	1.95	1.87
Heptanoic	7		2.43

Table 2
Relationships between log P and the number of carbon atoms for C_2–C_6 monocarboxylic aliphatic acids for chloroform–water and diethyl ether–water (data from [14])

Solvent	Slope a	Intercept b	n	r^2
Chloroform	0.6032	−2.7118	11	0.9885
Diethyl ether	0.5620	−1.5020	5	0.9946

Log $P = ax + b$, where x = number of carbon atoms.

Table 4
Peak areas from successive extractions of the same VFA mixture with fresh ether phase

Acid	Peak area for extraction No. (arbitrary units)			Amount of compound		
				Found by GC		Label value (mg C/l)
	1	2	3	μmol	mg C/l	
Acetic	1622	1118	827	0.601	1442	1369
Propionic	579	211	73.8	0.045	160.7	180.2
Isobutyric	1226	168	N.D.	0.047	226.3	240.2
Butyric	1193	176	N.D.	0.046	220.5	240.2
Isovaleric	1766	113	N.D.	0.048	290.7	300.3
Valeric	1763	105	N.D.	0.048	290.1	300.3
Isocaproic	2210	73.4	N.D.	0.053	379.1	360.3
Caproic	2252	73.5	N.D.	0.053	381.9	360.3
Heptanoic	2362	80.6	N.D.	0.053	446.4	420.4
Total VFA (mg C/l) (sum of individual compounds)					3838	3771
Total VFA (mg C/l) (using carbon analyzer)					3801	

The amount of compound found was calculated using the first injection data, and the concentrations of the individual compounds are also shown (Label value). N.D. = Not detectable.

The first extraction was incomplete for all the VFAs, particularly the C_2, C_3 and C_4 VFAs. The C_4 VFAs may not be a problem as their slope match the solid line in Fig. 2, and the extractions were approximately 95% or better for the higher VFAs. After the first extraction, 28.6% acetic acid and 64.3% propionic acid were recovered in the organic phase, which corresponds to $P = 0.4$ ($\log P = -0.398$) and $P = 1.8$ ($\log P = 0.255$), respectively. If the slopes of the calibration curves are corrected for 100% extraction efficiency for these two compounds, the values would match the linearity model (▲ in Fig. 2). This approach would suggest that all the extractions for C_2 and C_3 VFAs should be corrected to 100% efficiency, which may add one extra step in data manipulation. However, if the standards are rigorously manipulated in the same way as the samples in the preparation step, and if the precision is consistent and within reasonable limits (in our case $< 5\%$), then such a correction factor is not necessary. Therefore, analysts must be aware of these limitations, because the accuracy may suffer, especially if the extractions are not repeatable.

4. Conclusions

Potential limitations on the analysis and the calibration procedures were found with the GC analysis of VFAs using liquid–liquid extractions. This could affect the precision and accuracy of the results. We have reported a consistent precision with good reproducibility (1–5%). We have used the carbon analyzer as an independent method to ensure the accuracy of the calibration, and concluded that our current calibration method is satisfactory. Analysts using this method can calibrate their instruments using liquid–liquid extraction of standards, provided that the samples and the standards are rigorously treated in the same way.

Acknowledgements

We thank M.K. Haas who has installed the GC system and started the work on this method. We also thank S. Elchuk for technical comments, G.F. Keenleyside for editorial suggestions and H.A. Cox for graphic art expertise.

References

[1] F. Caron, *TR-560* (also available as *COG-93-100*), Atomic Energy of Canada, Chalk River, 1994 (unpublished report, available from Scientific Documents Distribution Office, Chalk River Laboratories, Chalk River).
[2] A.J. Weiss, A.J. Francis and P. Colombo, in M.W. Carter (Editor), *Management of Low-Level Radioactive Waste, Atlanta, GA, 1977*, Pergamon Press, New York, 1979, p. 747.
[3] A.J. Francis, C.R. Iden, B.J. Nine and C.K. Chang, *Nucl. Technol.*, 50 (1980) 158.
[4] J.B. Gillow and A.J. Francis, *BNL–45756*, Department of Energy, Brookhaven National Laboratory, Upton, NY, 1990.
[5] H.J. Ehrig, *Waste Manag. Res.*, 1 (1983) 53.
[6] C. Oman and P.A. Hynning, *Environ. Pollut.*, 80 (1993) 265.
[7] D.J. Lisk, *Sci. Tot. Environ.*, 100 (1991) 415.
[8] D.W. Rhodes, *Soil Sci. Am. Proc.*, 21 (1957) 389.
[9] K.J. Hauser and R.J. Zabransky, *J. Clin. Microb.*, 2 (1975) 1.
[10] *GC Bulletin 751G*, Supelco, Bellefonte, PA, 1982.
[11] *GC Bulletin 748H*, Supelco, Bellefonte, PA, 1985.
[12] *GC Bulletin 856*, Supelco, Bellefonte, PA, 1990.
[13] G.D. Christian and J.E. O'Reilly, *Instrumental Analysis*, Allyn & Bacon, Boston, MA, 2nd ed., 1986.
[14] C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley-Interscience, New York, 1979.