APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 6, 147–153 (1992)

Liquid–solid extraction of butyltin compounds from marine samples

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Environmental damage due to organotins (TBT, DBT, MBT) released from antifouling paints is well documented. The concentrations of these compounds in seawater are usually at ppt (parts per 10^{12}) levels. Many analytical techniques, including chromatographic and spectrophotometric ones, have been presented in the literature to detect organotins at these low levels. Liquid–liquid extraction is commonly employed as a concentration method. However, it presents some disadvantages during sampling campaigns and requires large volumes of toxic and expensive solvents. In this paper we propose an analytical method based on a liquid–solid extraction procedure that can be easily performed in the field and is characterized by good recoveries and high enrichment factors. Three different solid phases (Carbopack, LC 8 and LC 18) and five different eluting agents (methanol/tropolone, methanol, dichloromethane, hexane and diethyl ether) were evaluated. Carbopack and LC 18 were the most suitable solid phases. Inorganic tin was not retained on these solid phases and a separation of TBT from DBT and MBT was achieved, performing the elution in two steps with methanol and methanol/tropolone. In this way GF AA was suitably employed to obtain butyltin speciation data.

Keywords: Butyltin compounds, liquid–solid extraction, Carbopack, LC 18, GF AA, seawater, speciation

INTRODUCTION

Antifouling paints are the main source of tributyltin (TBT) in the marine environment.

In water, TBT is degraded to the less toxic dibutyltin (DBT) and monobutyltin (MBT)[1-3] and accumulates in marine organisms with high bioconcentration factors.[4-10]

Due to its high toxicity, TBT can induce deleterious effects on these non-target organisms, some of which are very important from an economical point of view, such as in mussels and oysters. Such effects were observed first in France[11,12] but have also been recorded in the UK[13] and in Portugal[14] despite the very low concentration of TBT detected in water samples collected in the same sites (ppt levels, i.e. parts per 10^{12}). Due to this fact, the use of TBT in antifouling paints was regulated in many countries; in the UK, the environmental quality target value was set at 20 ng dm^{-3} in 1987.[15]

Many analytical methods were developed in recent years to detect TBT and its degradation products down to the ppt level. These methods include the use of chromatographic[16-21] and spectrophotometric[21-27] instrumentation as detection techniques.

Most of these need a preliminary step to separate butyltins from the matrix to avoid matrix interferences and to concentrate butyltins in order to render them detectable. Usually, a liquid–liquid extraction is employed because of very good recoveries and high enrichment factors.

However, this kind of extraction presents some disadvantages: for example, it is time-consuming, handling is laborious, there is a potential health hazard (large volumes of organic solvents are used) and, last but not least, it is difficult to perform in the field and on oceanographic ships during sampling campaigns. In this case, the samples are generally stored and the extraction is performed later. Nevertheless, during sample storage, analyte losses and degradation processes could occur, altering the butyltin speciation in the samples.

Recently, adsorption of TBT on liquid–solid extraction discs from water samples has been studied successfully.[28-30] In the last few years we have carried out a study to optimize an analytical method based on a liquid–solid extraction (LSE)

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0268-2605/92/020147-07 $05.00

Received 30 December 1991

procedure able to be easily performed in the field and on oceanographic ships during sampling campaigns. The procedure was characterized by good recovery and high enrichment factors.

EXPERIMENTAL

Materials

Organic solvents were 'RS–pesticide grade' from Carlo Erba; tropolone (2-hydroxycycloheptatrienone) was from Lancaster Synthesis; nitric acid, potassium dichromate and tributyltin chloride (TBT) were from BDH; dibutyltin chloride (DBT) and monobutyltin chloride (MBT) were from Aldrich; Sn(IV) 'Titrisol' standard solution was from Merck; SPE LC 18, SPE LC 8 extraction tubes and Carbopack B 80–120 mesh were obtained from Supelco.

The organotin stock solutions ranging from 0.2 (TBT) to 0.5 (MBT) mg cm^{-3} (as Sn) concentration were prepared gravimetrically in methanol and diluted 1000-fold to give the working standard solutions. When stored refrigerated in the dark, stock solutions are stable for at least three months and the working solutions for at least one week, but the latter were renewed daily.

Apparatus

A Varian Spectra AA 40 P double-beam atomic absorption spectrometer fitted with deuterium background correction and with peak height measurement facilities was used for all absorption measurements. Sample solutions were introduced in pyrolytic graphite tubes by a Varian Autosampler model PSD 96.

Absorption signals were obtained by the argon stopped-flow method. A hollow-cathode lamp was employed at a current of 7 mA. The other operating conditions were the following: wavelength 286.3 nm; gas flow (argon) 2 dm^3 min^{-1}; spectral bandpass 0.5 nm; measurement time 2 s; injected volume 20 µl.

The GF AA thermal programme was optimized by us and consists of drying with a temperature ramp from 75 to 120 °C in 80 s, charring with a temperature ramp from 120 to 600 °C in 30 s, and atomization for 2 s at 2600 °C.

A matrix modifier ($K_2Cr_2O_7/HNO_3$, 0.04%/0.5% in water, w/v) was automatically introduced, together with the sample, in a single 20-µl injection by a Varian autosampler. The GF AA signal so enhanced obeyed Beer's law from 0.2 to 2 ng of tin, with a detection limit of 0.2 ng of tin (signal = five times that of noise). Calibration curve data are reported in Table 1.

Table 1 Calibration curve data and detection limits for inorganic tin and butyltin compounds

	Linearity range (ng)	Sensitivity (abs/ppm)	*Y*-intercept (abs × 10^2)	Correlation coefficient	Detection limit (ng)
TBT	0.2–2	9.85	1.52	0.997	0.2
DBT	0.2–2	9.32	2.20	0.998	0.2
MBT	0.2–2	9.41	4.04	0.998	0.2
Sn(IV)	0.2–2	8.03	1.32	0.997	0.2

Some analyses were also performed by GC FPD. The apparatus and the procedure have been described elsewhere.[20]

Extraction optimization

Adsorption tests

Adsorption capacities were tested by adding known volumes (10 cm^3) of TBT, DBT and MBT standard solutions (10 ppm) to each solid phase. The columns were always conditioned with 10 cm^3 of methanol and 10 cm^3 of distilled water, carefully avoiding dryness. The solutions were passed through the columns by vacuum and analysed by GF AA. No difference between the sample signal after passage through the column and the blank signal indicated quantitative retention. The test was continued until a significant concentration, indicating no quantitative retention, was detected.

The flow rate was always 10 cm^3 min^{-1} as a result of a study of the optimization of this parameter.

For each butyltin compound and for each solid phase the adsorption test was repeated three times.

Elution tests

Before the conditioning step, a washing step was performed with the eluting agent to remove impurities soluble in it. In fact, a number of organic compounds may be extracted from SPE tubes[31] interfering in the following determination, especially if it is performed by GC FPD. The nature and the number of these potentially interfering compounds depend on the different kinds of commercial cartridges.[30] The washing and the conditioning solutions were analysed, as blanks, for butyltins; no signals were obtained either in AA or GC FPD. Different solutions (10 cm^3) containing 100 ng of TBT, DBT or MBT respectively were passed through the columns. The columns were dryed under vacuum. The analytes were eluted with successive aliquots (2 cm^3) of the eluting agent. The elution was performed with a 'Visiprep' solid phase extraction vacuum manifold by Supelco, allowing us simultaneously to work with up to 12 cartridges with an accurate vacuum control. The elution rate was always 2 cm^3 min^{-1}. The maximum elution volume investigated was 10 cm^3.

After elution the volume of the organic phase was concentrated down to 1 cm^3 in a thermostated water bath (35 °C) under a gentle stream of nitrogen and analysed by GF AA. For each eluting agent and for each butyltin compound the elution test was repeated five times.

After these tests, LC 8 was rejected, due to the larger volumes needed to elute butyltins from it.

Recovery tests

Recovery tests were carried out on deionized water and on spiked seawater samples.

Different volumes of deionized water (ranging from 50 cm^3 to 1000 cm^3) containing 100 ng of TBT, DBT and MBT respectively, were passed through the columns and the butyltins were eluted and analysed according to the procedure described above. For each volume and for each butyltin compound the test was repeated twice.

Uncontaminated water samples, collected in the Tyrrhenian Sea, were spiked with 50 ng of TBT, 25 ng of DBT and 25 ng of MBT. The samples were collected in the open sea and analysed for butyltins by an analytical procedure described by us elsewhere,[20] consisting in a liquid–liquid extraction followed by a derivatization with pentylmagnesium bromide, a clean-up step on silica gel and a GC FPD determination, resulting in a butyltins concentration of below 2 ng dm^{-3}. One litre (1 dm^3) was passed through the Carbopack column and 250 cm^3 through the LC 18 column.

The test was repeated four times for both Carbopack and LC 18.

Procedure

The optimized procedure can be summarized as follows.

A known volume of seawater sample (250 cm^3 for LC 18 and 1000 cm^3 for Carbopack) is passed, by a water vacuum pump, through the SPE cartridges (containing 100 mg of Carbopack or 500 mg of LC 18) previously conditioned with 10 cm^3 of methanol and 10 cm^3 of distilled water, at 10 cm^3 min^{-1} flow rate.

Then, after washing with 10 cm^3 of distilled water to remove matrix salts, TBT is eluted with the Supelco apparatus (at a flow rate of 2 cm^3 min^{-1}) with 2 cm^3 of methanol, and successively DBT + MBT with 2 cm^3 of methanol/tropolone (300 mg of tropolone in 1 dm^3 of methanol).

The sample volume is reduced to 1 cm^3 in a thermostated water bath (35 °C) under a gentle stream of nitrogen and the solution is then analysed.

In the case of GC FPD, which does not need a previous separation, the elution is performed directly with methanol/tropolone eluting all the butyltin compounds at the same time.

RESULTS AND DISCUSSION

The aim of this research was the optimization of a simple procedure for the extraction in the field of butyltins from seawater samples.

AA was chosen as the measurement technique, during the optimization study, because of its easy handling and short analysis time.

The study was carried out in order to determine the adsorption capacity of solid phases, and the recovery and the enrichment factors obtainable with this kind of extraction.

Adsorption tests were carried out with TBT, DBT, MBT and inorganic tin (SnIV) respectively.

On each solid phase (Carbopack, LC 8 and LC 18), inorganic tin was not retained at all, whilst the retention of organic tin was excellent. In fact, butyltins were completely retained on Carbopack, to the extent of up to 1 mg of butyltin compound per gram of solid phase and up to 6 mg g^{-1} on LC 8 and LC 18, as shown in Table 2.

Elution tests were carried out for TBT, DBT and MBT respectively, with five eluting agents (methanol/tropolone, methanol, dichloromethane, hexane and diethyl ether). The results obtained on Carbopack and on LC 18 are shown in Table 3. As it can be seen, both for Carbopack and LC 18, diethyl ether, hexane and dichloromethane were not able to elute any butyltin compound; methanol was able to elute TBT only (no

Table 2 Butyltins retention test
The results, expressed as percentages, are the averages of three different tests

	1 mg g^{-1}		3 mg g^{-1}		5 mg g^{-1}		6 mg g^{-1}	
	Carbopack	LC 18 and LC 8	Carbopack	LC 18 and LC 8	Carbopack	LC 18 and LC 8	Carbopack	LC 18 and LC 8
TBT	100	100	100	100	95	100	—[a]	100
DBT	100	100	95	100	80	100	—	100
MBT	95	100	75	100	50	100	—	100

[a] —, not tested.

Table 3 Butyltins elution test from Carbopack and LC 18
The results, expressed as percentages, are the averages of five different experiments

	Methanol/tropolone		Methanol		Dichloromethane		Hexane		Diethyl ether	
	Carbopack	LC 18	Carbopack	LC 18	Carbopack	LC 18	Carbopack	LC 18	Carbopack	LC 18
TBT	105 ± 7	94 ± 7	105 ± 4	96 ± 8	27 ± 8	< 10	< 10	0	0	0
Elution volume	2 cm^3	2 cm^3	2 cm^3	4 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3
DBT	102 ± 9	101 ± 5	0	0	0	0	0	0	0	0
Elution volume	2 cm^3	2 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3
MBT	107 ± 5	89 ± 4	0	0	0	0	0	0	0	0
Elution volume	4 cm^3	2 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3	10 cm^3

Table 4 Butyltins recovery test from deionized water
The results, expressed as percentages, are the averages of two determinations
The matrix was deionized water containing 100 ng of TBT, DBT and MBT respectively

	100 cm^3		250 cm^3		500 cm^3		1000 cm^3	
	Carbopack	LC 18	Carbopack	LC 18	Carbopack	LC 18	Carbopack	LC 18
TBT	100	95	100	92	96	62	93	24
DBT	101	92	95	88	96	—	90	—
MBT	93	88	91	84	92	—	88	–

[a] —, not tested.

Table 5 Butyltins recovery test from spiked seawater samples
The results, expressed as percentages, are the averages of four determinations

	Carbopack				LC 18			
	AA		GC FPD		AA		GC FPD	
	Spike (ng)	Recovery (%)	Spike (ng)	Recovery (%)	Spike (ng)	Recovery (%)	Spike (ng)	Recovery (%)
TBT	50	97 ± 3	50	100 ± 2	50	91 ± 7	50	102 ± 2
DBT			50	98 ± 15			50	98 ± 6
DBT + MBT	25 + 25	92 ± 6			25 ± 25	90 ± 6		
MBT			50	98 ± 10			50	94 ± 8

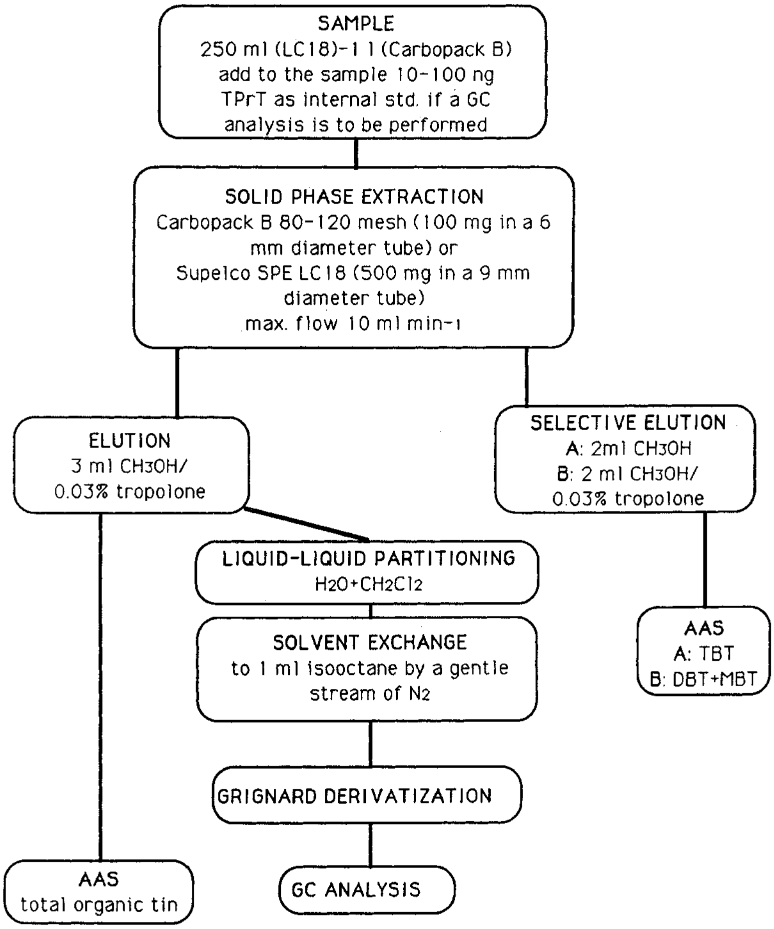

Figure 1 Flow chart of analytical procedure.

elution was observed for DBT and MBT) and methanol/tropolone was able to elute completely all the butyltin compounds at the same time. Thus, it is possible to obtain a separation between TBT and its degradation products performing the elution in two steps: firstly with methanol, eluting TBT only, and then with methanol/tropolone, eluting the remaining butyltin compounds. The same results were obtained on LC 8 but, in this case, larger volumes of eluents (about $10\,\mathrm{cm}^3$) were needed. Therefore, the following recovery tests were carried out on Carbopack and LC 18 only.

To determine the influence of the sample volume on the retention, different volumes of butyltin standard solutions, ranging from $100\,\mathrm{cm}^3$

Table 6 Determination of butyltins in the Venice Lagoon by LSE on Carbopack
Sample volume: $1000\,\mathrm{cm}^3$. The results are expressed in ppt (parts per 10^{12})

	Point 1		Point 2		Point 3		Point 4	
	AA	GC FPD	AA	GC FPD	AA	GC FPD	AA	GC FPD
TBT	<10	10	<10	9	<10	11	<10	<2
DBT		4		12		6		<2
	37[a]		38[a]		35[a]		<10[a]	
MBT		17		13		23		<2

[a] The sum of MBT and DBT.

to 1 dm^3, were prepared. The results are shown in Table 4. The retention on Carbopack was always satisfactory, showing no significant effect of the sample volume on LSE efficiency; on the contrary, on LC 18 good retention was obtained only up to 250 cm^3 for TBT, whilst for larger volumes the retention was very poor. DBT and MBT were affected from the volume of the sample more than TBT, probably because of their higher polarity. Due to these results the optimum sample volume was chosen to be 1 dm^3 for Carbopack and 250 cm^3, as a compromise between high recovery and the need for high enrichment factors, for LC 18. The procedure was also checked on uncontaminated spiked seawater samples.

Both AA and GC FPD were employed for butyltin measurement.

After liquid–solid extraction (LSE), different elutions were carried out depending on the detection technique: for AA measurement the elution was performed in two steps with methanol followed by methanol/tropolone; for GC FPD measurement the elution was performed in a single step directly with methanol/tropolone. The recoveries, shown in Table 5, were always higher than 90% both on Carbopack and LC 18, and the agreement between the techniques was excellent. During this test, DBT and MBT recoveries were slightly higher than those observed during the previous experiments. The influence of the salt matrix and the difference of pH, between distilled water and seawater, on LSE efficiency could explain these results.

Figure 1 shows the flow diagram of the proposed procedure. After liquid–solid extraction, elution in two steps with methanol and methanol/tropolone followed by AA measurement gives the TBT and DBT + MBT concentrations. On the other hand, elution in a single step with methanol/tropolone gives the total butyltins concentration if followed by AA measurement, or the whole butyltin speciation if followed by GC FPD analysis.

Finally, the whole procedure was checked in the field during two sampling campaigns carried out in the Venice Lagoon and on an oceanographic ship in the Adriatic Sea.

The samples collected in the Adriatic Sea always had concentrations below the detection limit of both the techniques employed (10 ng dm^{-3} for AA and 2 ng dm^{-3} for GC FPD). Nevertheless, liquid–solid extraction was easily performed during adverse meteorological conditions, resulting in a very satisfactory procedure from an operational point of view.

Samples collected at four points in the Venice Lagoon were passed through Carbopack SPE and analysed by AA, after elution in two steps, and by GC FPD, after elution in a single step.

The results are shown in Table 6. At sampling point No. 4 the butyltins were below the detection limit of both techniques. In the other three points, TBT was always below the detection limit of AA, but it was detected by GC FPD. On the contrary, DBT and MBT were detected by both the techniques. The agreement between the techniques was very good, considering the very low butyltins concentration found.

CONCLUSIONS

Three different solid phases (Carbopack, LC 8 and LC 18) and five different eluting agents (methanol/tropolone, methanol, dichloromethane, hexane and diethyl ether) were evaluated. Carbopack and LC 18 as solid phases and methanol and methanol/tropolone as eluting agents were the most suitable. Inorganic tin was not retained at all on these solid phases and a separation of TBT from DBT and MBT was achieved by performing the elution in two steps with methanol and methanol/tropolone. In this case GF AA was suitably employed to obtain data on partial butyltin speciation. Otherwise, performing the elution in a single step with methanol/tropolone, data on the total butyltins content or on butyltin speciation are obtained employing GF AA or GC FPD respectively.

Liquid–solid extraction of butyltin compounds from seawater is characterized by very good recovery (always about 90%) and, as the final extract volume is 1 cm^3, by enrichment factors ranging from 250 on LC 18 to 1000 on Carbopack. The final volume can be further reduced, carefully avoiding dryness, achieving higher enrichment factors.

Even if both Carbopack and LC 18 gave satisfactory results, Carbopack seems to give better performances due to higher enrichment factors.

The extraction apparatus is very simple and it is able to operate automatically with many samples simultaneously in the field also.

Only small volumes of organic solvents (a few cubic centimeters) are needed, reducing the potential adverse effects on the operator's health.

As a conclusion, liquid–solid extraction seems to be a good alternative to liquid–liquid extraction, especially during sampling campaigns carried out far away from laboratories.

Acknowledgement We gratefully acknowledge Mr A Perini for general assistance during some of the experiments.

REFERENCES

1. Blunden, S J and Chapman, A H *Environ. Tech. Lett.*, 1982, 3: 267

2. Maguire, R J, Carey, J H and Hale, E J *J. Agric. Food Chem.*, 1983, 31: 1060

3. Seligman, P F, Valkirs, A O and Lee, R. F *Environ. Sci. Technol.*, 1986, 20: 1229

4. Chiavarini, S, Cremisini, C and Morabito, R In: *Proceedings of the FAO/UNEP/IAEA Consultation Meeting on the Accumulation and Transformation of Chemical Contaminants by Biotic and Abiotic Processes in the Marine Environment*, Lerici, 24–28 September 1990, Gabrielides, G P (ed), 1991, pp 179–187

5. Caricchia, A M, Chiavarini, S, Cremisini, C, Morabito, R and Scerbo, R *Analyt. Sci.*, 1992, 7: in press

6. Zuolian, C and Jensen, A *Mar. Polut. Bull.*, 1989, 20: 281

7. Laughlin, R B, French, W and Guard, H E *Environ. Sci. Technol.*, 1986, 20: 884

8. Beaumont, A R and Budd, M D *Mar. Pollut. Bull.*, 1984, 15: 402

9. Lawler, I F and Aldrich, J C *Mar. Pollut. Bull.*, 1987, 18: 274

10. Stromgren, T and Bongard, T *Mar. Pollut. Bull.*, 1987, 18: 30

11. Alzieu, C, Héral, M, Thibaud, Y, Dardignac, M J and Feuillet, M *Rev. Trav. Inst. Pêches Marit.*, 1983, 45: 101

12. Alzieu, C, Sanjuan, J, Deltreil, J P and Borel, M *Mar. Pollut. Bull.*, 1986, 17: 494

13. Waldock, M J and Thain, J E *Mar. Pollut. Bull.*, 1985, 14: 411

14. Quevauviller, Ph, Labigne, R, Pinel, R and Astruc, M *Environ. Pollut.*, 1989, 57: 149

15. Waldock, M J, Thain, J E and Waite, M E *Appl. Organomet. Chem.*, 1987, 1: 287

16. Matthias, C L and Bellama, J M *Environ. Sci. Technol.*, 1986, 20: 609

17. Maguire, R J and Huneault, H *J. Chrom.*, 1981, 209: 458

18. Müller, M D *Fr. Z. Anal. Chem.*, 1984, 317: 32

19. Chiavarini, S, Cremisini, C, Ferri, T, Morabito, R and Perini, A *Sci. Tot. Environ.*, 1991, 101: 217

20. Caricchia, A M, Chiavarini, S, Cremisini, C, Fantini, M and Morabito, R *Sci. Tot. Environ.*, in press

21. Ashby, J R and Craig, P J *Appl. Organomet. Chem.*, 1991, 5: 173

22. Müller, M D *Anal. Chem.*, 1987, 59: 617

23. Han, J S and Weber, J H *Anal. Chem.*, 1988, 60: 316

24. Randall, L, Donard, O and Weber, J H *Anal. Chim. Acta*, 1986, 184: 197

25. Donard, O, Rapsomanikis S and Weber, J H *Anal. Chem.*, 1986, 58: 772

26. Pinel, R, Benabdallah, M Z, Astruc, A, Potin-Gautier, M and Astruc, M *Analusis*, 1984, 12: 344

27. Parks, E J, Blair, W R and Brinckman, F E *Talanta*, 1985, 32: 633

28. Junk, G A and Richard, J J *Chemosphere*, 1987, 16: 61

29. Junk, G A and Richard, J J *J. Res. Natl. Bur. Stand.*, 1988, 93: 274

30. Evans, O, Jacobs, B J and Cohen, A L *Analyst (London)*, 1991, 116: 15

31. Junk, G A, Avery, M J and Richard, J J *Anal. Chem.*, 1988, 60: 1347