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GAS CHROMATOGRAPHIC ANALYSIS OF THE EXTRACTION SOLVENT USED IN NUCLEAR FUEL REPROCESSING PLANTS

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SUMMARY

Gas chromatography is useful for the analysis of the complexing agent (tributyl phosphate) and the diluent (hyfrane) which constitute the extraction solvents used in nuclear fuel reprocessing plants. Analyses were carried out to determine the composition of the solvents at different points in the extraction circuit, and the tributyl phosphate content of the plant waste products.

INTRODUCTION

One method of reprocessing irradiated nuclear fuels is selective complexing of the elements to be recovered (U, Pu) and extraction of the complexes formed using an organic phase. In French reprocessing plants the complexing agent chosen is tributyl phosphate (TBP) and the separation is carried out by liquid–liquid extraction between a solution of the used fuel in nitric acid and an organic phase flowing in the opposite direction. The organic phase is a solution of TBP (30%, v/v) in hyfrane, a complex mixture of saturated hydrocarbons obtained by polymerization of propylene and hydrogenation of the tetramer formed[1,2].

The complexing and partition equilibria are influenced by various factors, in particular the nature of the organic phase, the pH of the aqueous phase and the concentrations of the different species in both phases. In order to obtain a better yield, the nuclear fuel is subjected to ever-increasing temperatures and activities which, during the reprocessing, cause extensive radiolysis leading to the rapid degradation of the solvent and to decrease in its efficiency. In particular, TBP is decomposed into the dibutyl phosphate and then into monobutyl phosphate.

Regular analyses carried out periodically and at different points on the reprocessing circuit are therefore indispensable to control the composition of the solvent and, if necessary, to optimize the yield of the operations by correcting the composition of the adjacent phases. Gas chromatography (GC) was chosen for these controls because it is a simple, rapid and reliable method which is easily automated and

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can therefore be used in a radioactive environment. In addition, its high sensitivity should enable control of TBP pollution in the plant waste.

EXPERIMENTAL

Chemical reagents

The diluents hydrane and hydrogenated tetrapropylene (TPH) were obtained from Hyfrane Company (France) and Elf Company (France) respectively, tributyl phosphate from Protex (France), Fluka (Switzerland) and BDH (U.K.) and triisobutyl phosphate from Marsan (Monaco).

Apparatus

Two Intersmat chromatographs (Delsi, France) were used. The IGC 16 model with programmable temperature control is fitted with a thermal conductivity detector and two flame ionization detectors which can be transformed into thermoionic detectors. The more recent IGC 121 DFL model, incorporating a microprocessor and flame ionization detectors, is used for the capillary column assemblies because of its two injection systems ("on column" and with flux divider). This apparatus can be connected to an automatic sampler (GC 111, Delsi) and computer-integrator (Enica 10, Delsi).

Packed columns were prepared in the laboratory from stainless-steel or glass tubes of internal diameter between 3.5 and 4 mm. Glass capillary columns were also prepared in the laboratory; the fused-silica column was supplied by Chrompack. The carrier gas used was helium with flow-rates of the order of 20 ml/min and 2 ml/min for the packed and capillary columns respectively.

The coupling between the chromatograph and mass spectrometer was made using a Varian 3700 chromatograph designed to receive capillary columns and a mixed-ion-source Varian spectrometer (electronic or chemical ionization). The data from the photomultiplier were processed by a MAT SS 20 system.

RESULTS

Quality control of the hyfrane

Hyfrane is a complex mixture of saturated hydrocarbons whose boiling points are between 160 and 240°C. The efficiency of the packed columns is not sufficient to separate these mixtures and we chose a WCOT type capillary column which represents a compromise between efficiency and capacity. The column (50 m × 0.3 mm I.D.) was coated with methylsilicone SE-30. It has an efficiency of 109 000 plates for *n*-dodecane.

The operating conditions were chosen so as to obtain the best separation of a mixture of C_8–C_{12} *n*-alkanes. A small quantity of this mixture was added as internal standard to the hyfrane sample. The chromatogram in Fig. 1. shows approximatively 60 peaks, a large number of which cannot be well resolved. These analytical conditions are however sufficient to distinguish between hyfrane samples from different origins.

The use of a fused-silica column (50 m × 0.23 mm I.D.) coated with methylsilicone SIL 5, with a greater efficiency of 142 000 plates, gave good resolution of

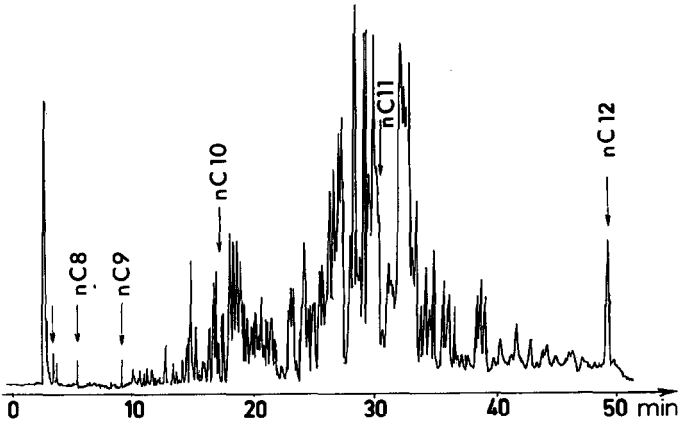

Fig. 1. Analysis of crude hyfrane with the addition of traces of *n*-alkanes. Conditions: WCOT glass column (50 m × 0.32 mm I.D.), phase SE-30, temperature programmed at 1°C/min from 60°C; flame ionization detector, 200°C; injection port, 150°C; carrier gas (helium) flow-rate, 2 ml/min.

more than 150 peaks on the chromatogram (Fig. 2). The latter is a real "fingerprint" of the hyfrane and facilitates its monitoring during the reprocessing cycles.

In order to identify the constituents of hyfrane, we coupled the chromatographic column to a mass spectrometer. Considerable similarity between the response of the flame ionization detector (Fig. 2) and the total ionic current from the spectrometer (Fig. 3) can be observed. The selection of ion currents at masses 142, 156, 170 and 184 enables the elution of alkanes $C_{10}H_{22}$ to $C_{13}H_{28}$ to be monitored. The presence of peaks with m/e = 142 beyond spectrum no. 400 corresponds to the fragmentation of alkanes with 11, 12 and 13 carbon atoms. A similar phenomenon, but less apparent, is revealed by the peaks of masses 142 and 156. In so far as this fragmentation and the ionization energy remain small (less than 80 eV), the propor-

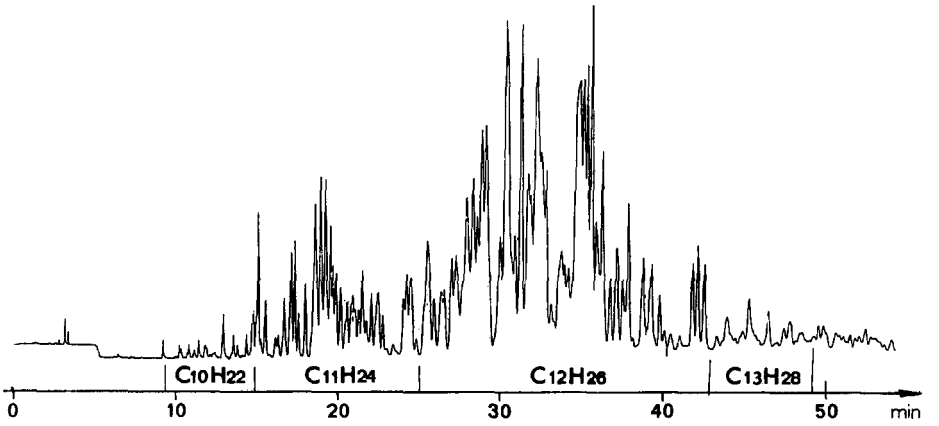

Fig. 2. Analysis of crude hyfrane. Conditions: WCOT fused-silica column (50 m × 0.23 mm I.D.), phase SIL 5, temperature programmed at 0.2°C/min from 65°C; flame ionization detector, 200°C; injection port, 150°C; carrier gas (helium) flow-rate, 1 ml/min.

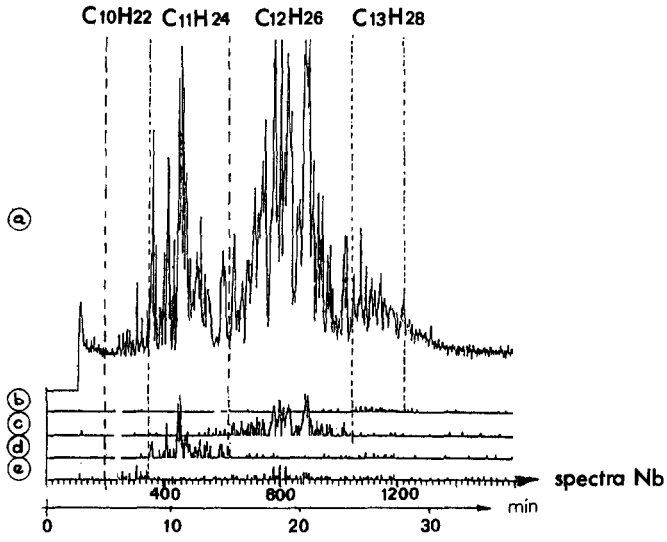

Fig. 3. Gas chromatography–mass spectrometry for the analysis of hyfrane. Chromatographic conditions as in Fig. 2. a, Total ion current; b, current at *m/e* 184; c, current at *m/e* 170; d, current at *m/e* 152; e, current at *m/e* 142.

tions of the C_{10}–C_{13} alkanes can be determined after their regions of elution have been located on the chromatogram and by taking into account the response coefficients for normal alkanes. The results obtained for both types of hyfrane are given in Table I.

TABLE I

DISTRIBUTION OF ALKANES IN COMMERCIAL DILUENTS

Alkane	*Retention time (min)*	*Concentration (mole %)*	
		Hyfrane	*TPH*
$C_{10}H_{22}$	10–15	1.6	1.5
$C_{11}H_{24}$	15–22	20.5	14.5
$C_{12}H_{26}$	22–37	53.6	67.3
$C_{13}H_{28}$	37–50	15.4	12.2
$C_{14}H_{30}$	50–58	8.8	4.5

Quality control of tributyl phosphate

Industrial TBP is prepared by the reaction between phosphorus oxychloride and butanol in the presence of a base (pyridine) which eliminates the hydrochloric acid formed. The main impurities which can occur are butanol and various phosphorus compounds including dibutyl phosphate.

Fig. 4 shows the analysis of the Fluka TBP on a packed Carbowax 20M column. Contrary to observations made with a less polar phase, the tail of the TBP peak (14) is shorter and the resolution of the different constituents is satisfactory.

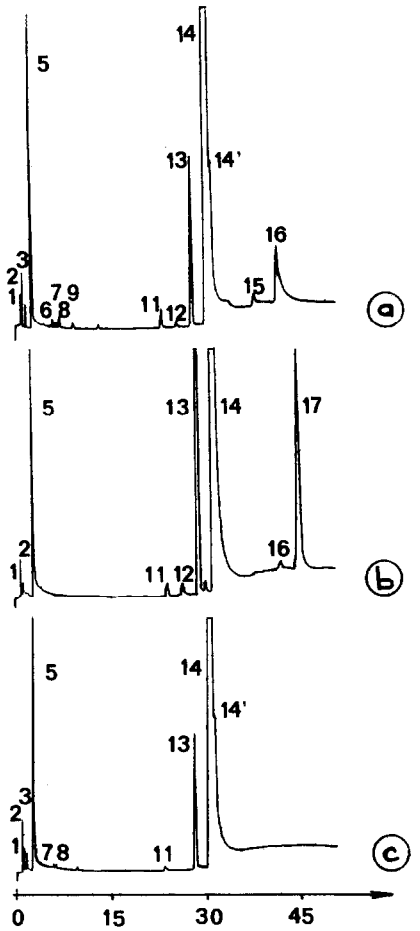

Fig. 4. Analysis of commercial TBP. Conditions: glass column (5 m × 3.5 mm I.D.), 5% Carbowax 20M on Chromosorb W HP, temperature programmed at 4°C min from 100°C; flame ionization detector, 300°C; injection port, 280°C; carrier gas (helium) flow-rate 20 ml/min. Origins of the TBP: a, Fluka; b, Protex; c, BDH.

The butanol (peak 5) can easily be identified by its retention time. The other constituents were identified by mass spectrometry. Using electronic ionization, peaks 1–4 and 8–10 (Table II) were easily identified as butanol derivatives. For the other peaks, both types of ionization were used. Peaks 11–13 correspond to TBP isomers. Triisobutyl phosphate, peak 11, was also identified by its retention time. As expected, the mono- and dibutyl phosphates, which are acid products of the TBP decomposition, are not eluted from the column. In addition, chromatographic analysis treads the significant differences between the TBP samples of different origins (Fig. 4).

The quantitative analysis of butanol was carried out directly. A calibration was obtained by using solutions of butanol in dodecane with *n*-decane as internal standard. The chromatographic conditions were identical to those of Fig. 4, except that the temperature of the column was maintained at 90°C until the butanol was

TABLE II

IMPURITIES ANALYSIS IN COMMERCIAL TBP

Peak No. (Fig. 4)	*Impurity*	*MW*	*TBP content*		
			BDH	*Fluka*	*Protex*
1	Chlorobutane	92	0.035	0.018	0.021
2	Di-*n*-butyl ether	130	*	0.025	0.024
3	Butyl propyl ketone	128	*	0.014	*
5	*n*-Butanol	74	0.97 0.64**	0.43 0.29**	0.44 0.35**
6	Dodecane	170	0.004	0.017	*
7	Not identified	174	0.007	0.002	*
8	1,1-Dibutoxybutane	202	0.006	0.011	0.002
9	2-*n*-Butoxyethanol	118	*	0.027	*
10	2-Ethylhexanol	140	0.008	0.016	*
11	Triisobutyl phosphate	266	0.014	0.056	0.056
12	Diisobutyl *n*-butyl phosphate	266	*	0.025	0.042
13	Isobutyl di-*n*-butyl phosphate	266	0.50	0.49	2.22
13	Not identified		*	*	0.02
14	Tributyl phosphate	266	98.32	98.34	95.73
14	$PO_4C_{13}H_{29}$	280	0.067	0.05	*
15	$PO_4C_{16}H_{35}$	322	0.031	*	*
16	Phosphate derivative	310	*	0.39	0.028
17	Dibutylphosphoramidate	209	*	*	1.20

* Below detection limit.

** From *n*-butanol as standard.

eluted. The accuracy is sufficient to distinguish between two samples of different origins. The averages obtained in this way for ten injections are 0.29 ± 0.01 and 0.35 ± 0.02 g% for the Fluka TBP and the Protex TBP respectively.

We carried out a quantitative estimation of the other impurities using the area of each peak and supposing the mass response coefficients to be identical to that of TBP. This approximation is justified for the phosphorus derivatives but is rather inaccurate for the more volatile components (1–10, Fig. 4). In addition, the calculation does not account for any impurities not eluted from the column, in particular water. The results, given in Table II, should therefore be used only to compare different samples.

Analysis of TBP in the reprocessing circuit

Organic phase analysis. Depending on the sampling point, the solvent can contain from 1 to 75% (v/v) TBP with the most common concentration being of the order of 30%. This phase can also contain TBP degradation products (10–500 mg/l and 1–50 mg/l of di- and monobutyl phosphate respectively), traces of nitric acid and possible fission products. We will consider here only the analysis of the 30% TBP solution, as the other solutions could be made up to this concentration by dilution or concentration. The determination of the acid degradation products is reported elsewhere[3].

The initial tests indicated the need to dilute the sample. The isooctane (boiling

point 99°C) chosen as solvent gives a better vaporization of the sample in the injection port of the chromatograph whilst preserving stability during the manipulations at room temperature. A dilution factor of 100 gives a more accurate determination of the injected quantity (1 μl), a decrease in the viscosity of the mixture and a considerable decrease in the activity of the samples in the case of plant solvents. Under these conditions, quantitative chromatographic analysis on a column packed with SE-30 phase leads to a high relative standard deviation, about 2.5% for a series of six injections of a laboratory sample. In addition, the application to real plant samples leads to aberrant results because of the presence of acidic components not eluted from the column.

These difficulties were overcome by using triisobutyl phosphate (TiBP) as internal standard and by following a very strict analytical procedure. The unknown mixture containing the TiBP was injected between two injections of standard solutions also containing TiBP and of concentrations either side of that of the unknown mixture. For each solution, three samples were taken and three injections were made for each of these samples. The results obtained under these conditions are given in Fig. 5 and in Table III. The relative standard deviation is often lower than 0.5% which represents a sufficient accuracy for the reprocessing plant operators. It should however be noted that these values were obtained by manual measurement of the TBP and TiBP peak heights and that considerable improvement should be obtained by using an electronic integrator.

The majority of the measurements on the 30% (v/v) TBP solvent must be carried out on solutions whose activity requires that they be manipulated in a glove-

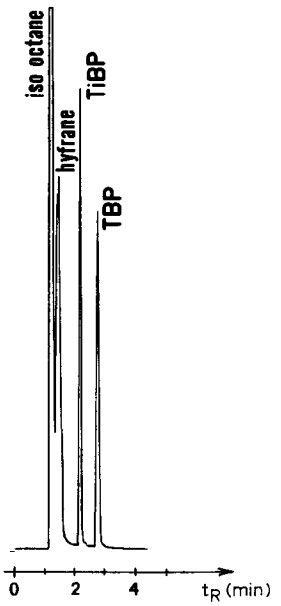

Fig. 5. Determination of the concentration of TBP in the reprocessing solvent. Conditions: glass column (3 m × 3.5 mm I.D.), 3% OV-1 on Chromosorb W HP, temperature 210°C; flame ionization detector, 300°C, injection port, 250°C; carrier gas (helium) flow-rate 20 ml/min.

TABLE III

TBP ANALYSIS IN THE REPROCESSING SOLVENT

Values are in % (v/v)

		Mean for three injections	*Overall mean*
Solution 1	Sample 1	30.12	30.3 ± 0.16
	Sample 2	30.48	
	Sample 3	30.31	
Solution 2	Sample 1	30.56	30.5 ± 0.10
	Sample 2	30.32	
	Sample 3	30.48	

box. It is then prohibited, for safety reasons, to use the flame ionization detector. We therefore tested the accuracy of the analyses obtained with a catharometer. The temperature of the detector was fixed at 300°C, the four WX filaments were subjected to a current of 150 mA and we operated at maximum sensitivity. Under these conditions, the limit of linearity for the response is determined as around 30 μg of TBP. We also confirmed that the response is not affected by the presence of TBP degradation products and nitrated derivatives contained in the real samples. The analysis of the 30% (v/v) TBP solution, using three injections for each of the six samples taken, led to a relative standard deviation of 0.7%. The method was also tested on samples with concentrations of the order of 3% (v/v) TBP and the accuracy obtained was approximately the same (0.5%).

Liquid chromatographic analysis as proposed by Chaussabel[4] and developed by Muller *et al.*[5] is also applicable to the analysis of radioactive solvents. The preparation of the samples without an internal standard is simpler, however the accuracy obtained is lower: ± 1.3% with solutions of 30% (v/v) TBP.

Aqueous phase analysis. The aqueous phase can, depending on the sampling point, contain TBP up to its saturation point (400 mg/l at room temperature) as well as variable concentrations of nitric acid, degradation products and fission products. We tried to approach the conditions for the chromatographic analysis described above by first extracting the TBP from the nitric acid solution by an organic solvent. According to the TBP concentration, partial evaporation of the solvent will be necessary before injection.

For the same reasons as mentioned above, we chose isooctane as solvent. In the initial tests, the internal standard TiBP was added to the sample solution before extraction. The results revealed a rapid decrease in the content of TiBP with time due to the degradation of this compound by the nitric acid. In order to avoid prolonged contact of the TiBP with the nitric acid phase, the internal standard was added to the isooctane. As this internal standard is no longer used as proof of extraction, we had to monitor its yield. This was approximately 98% when the extraction was carried out twice with 1 ml of isooctane for a 5-ml sample. A chromatographic test showed the high stability of the solutions prepared under these conditions.

The analyses were carried out with the same precautions as above (injection

of the sample between two standard solutions) and under the same conditions. Analysis of the TBP at concentrations between 5 and 400 mg/l is possible using a flame ionization detector. A considerable decrease in the detection limit (up to 100 μg/l) must be expected with a specific thermoionic detector (a flame ionization detector modified by the introduction of a rubidium bead in the flame) which favours the ionization of phosphorus compounds. The response of this detector is linear up to 135 mg/l of TBP. However, the positioning of the bead in the flame is a delicate operation and affects the detector resonse. During the analyses, a relatively fast pollution of the bead was also observed which leads to a decrease in sensitivity. It is therefore preferable to use the flame ionization detector for TBP concentrations higher than 20 mg/l and to concentrate solutions of lower concentration before analysis.

Control of pollution and separation of TBP wastes

TBP concentration in bitumen. When the extracting solvent (hyfrane–TBP) can no longer be used, it has such a high activity that it cannot be kept in liquid form. One of the methods used for its storage is encasement in bitumen. We attempted the analysis of TBP in these waste products by dissolving the solid samples and analysing the solution by GC. Among the solvents proposed by Stoller and Richards[6] and Burger[7], we chose carbon tetrachloride. Bitumen (4–5 g) taken from different points of the sample to safeguard against irregular diffusion of the TBP was dissolved in 100 ml of carbon tetrachloride solution containing 0.8 g/l TiBP as internal standard. It was not possible to introduce the almost coffee coloured solution obtained into a packed chromatographic column. Bearing in mind the sensitivity of the detector, 5 mg of TBP must be injected, that is 95 mg of bitumen in the case of a 5% encasement. The heavy components of bitumen rapidly pollute the column and lead to a decrease in its efficiency.

We therefore carried out chromatography on a glass capillary column impregnated with Carbowax 20M under the same conditions as for the analysis of TBP in the organic phase (see above). Injections of 0.1 μl of solution led to the results reported in Table IV. The accuracy obtained (around 1%), although much lower than for the analysis of 30% TBP, is sufficient for this type of control. After approximately 200 injections a slight colouration appeared over the first few decimetres of the col-

TABLE IV

TBP ANALYSIS IN BITUMEN

Values are in g%.

		Mean for three injections	*Overall mean*
Solution 1	Sample 1	2.86	2.82 ± 0.02
	Sample 2	2.80	
	Sample 3	2.81	
Solution 2	Sample 1	2.84	2.90 ± 0.04
	Sample 2	2.91	
	Sample 3	2.94	

umn leading to a decrease in its efficiency. The removal of this polluted part restored the original quality of the column.

The detection threshold is near 0.01 g% TBP in the bitumen.

TBP determination in waste waters. For environmental control of nuclear fuel reprocessing plants using TBP as extraction solvent or plastifier it is necessary to analyse traces of TBP in waste waters. The concentration of TBP in these effluents can be some μg per litre of water. It is therefore necessary to extract the TBP from a sample of large volume into a solvent in which TiBP has been added as internal standard. The extraction solvent should then be concentrated before the chromatographic analysis.

We chose hexane as the solvent and demonstrated that washing 500 ml of water twice with 25 ml of hexane each time extracts at least 99% of the TBP present. Before the chromatographic analysis, the hexane solution was concentrated in a Kuderna Danish apparatus. We confirmed that the reduction to 1 ml from 100 ml of pure hexane did not produce any peaks on the chromatogram which could disturb the TBP analysis and also that identical results were obtained after concentration of the extracts to 5 or to 1 ml.

The chromatographic analysis was carried out by injecting 1 μl of concentrate into a glass column filled with Chromosorb W HP impregnated with 5% (w/w) SE-30. These conditions are the same as for the analysis of TBP in the reprocessing solvent.

We tested the whole method with standard solutions of TBP in hexane at concentrations of 20–200 mg/l (in order to determine the linearity of the detector response in this range), and also with aqueous solutions of TBP containing 100, 248 and 495 μg/l. For these aqueous solutions the measured concentrations were 105, 250 and 520 μg/l respectively. The accuracy obtained (1–5%) is quite sufficient for this type of analysis. The chromatogram of 1 μl of concentrate, reduced from 5 ml, which was obtained from 500 ml of aqueous solution of TBP (concentration 100 μg/l), shows a TBP peak (at maximum sensitivity of the detector) 20 mm in height. It is therefore possible to determine much lower concentrations by increasing the volume of the sample (maximum 1 l), the solvent concentration (down to 1 ml) and the volume of concentrate injected. In this way the TBP concentration can be determined for solutions containing down to 5 μg TBP per litre of water.

CONCLUSIONS

The analytical methods proposed enable extracts from one end to the other of the nuclear fuel reprocessing line to be monitored. All our tests were carried out on non-radioactive solutions, but we endeavoured to operate under analytical conditions which can easily be met in "hot" laboratories.

The resolution obtained of the constituents of the diluent hyfrane, although incomplete, is satisfactory. The accuracy of the quantitative measurements of the alkane distribution enables us to observe successive creases in the number of carbon atoms of the constituents of the samples. If necessary, this "wear" could be compensated during the recycling of the solvent. Moreover, more intensive work on the importance of these degradation reactions could be envisaged, as well as on the rôle of the different hyfrane fractions in the reprocessing operations and with regard to the efficiency of the solvent extraction.

During a study on commercial TBP and TBP–hyfrane solutions, we were not able to determine the concentration of the radiolysis products, mono- and dibutyl phosphate, together with the other constituents. These non-volatile compounds cannot be directly eluted, but we were able to carry out their analyses by first performing a methylation reaction[3]. The accuracy determination of TBP present at 30% (v/v) in the solvent is of the order of that required for operating the plant (0.5%). Automation of the injections and examination of the chromatograms should improve this accuracy whilst simplifying the procedure.

With regard to the determination of traces of TBP in waste waters the permitted levels of pollution can only be set according to the sensitivity of the analytical methods. The constant demand for a decrease in the threshold level leads to the development of methods with increasingly higher levels of performance. The 5 μg/l limit reached here is undoubtedly only a step in this development.

REFERENCES

1 J. Lefevre, in O. Lesourd (Editor), *Guide International de l'Energie Nucléaire*, Paris, 1978, Ch. 8, p. 367.
2 J. Manelle and P. Regnaut, *Reprint from Economics of Nuclear Fuels*, International Atomic Energy Agency, Vienna, 1968.
3 C. Pommier and B. Marlet, in preparation.
4 L. Chaussabel, *Rapport CEA, DERDCA/DCAEA/SEA 79.230*, CEA, Fontenay-aux-Roses, 1979.
5 J. M. Muller, J. Cojean and A. Deloge, *Analusis*, 11 (1983) 271.
6 S. M. Stoller and R. B. Richards, *Reactor Handbook, Vol. 2, Fuel Reprocessing*, Interscience, London, 1961, p. 123.
7 P. Leroy, *Rapport CEA-SCCI 71*, CEA, Fontenay-aux-Roses, 1966.