Analysis of *n*-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide and TRUEX process solvent by gas and liquid chromatography

RALPH C. GATRONE*, PAUL G. RICKERT and E. PHILIP HORWITZ

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 (U.S.A.)

and

BARBARA F. SMITH, CATHERINE S. BARTHOLDI and AARON M. MARTINEZ

Chemistry and Laser Sciences Division, Los Alamos National Laboratory, Los Alamos, NM 87545 (U.S.A.)

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ABSTRACT

Complementary analytical procedures using capillary gas chromatography (GC) and high-performance liquid chromatography (HPLC) have been developed for the analysis of the TRUEX process solvents (CMPO–TBP–tetrachloroethylene or normal paraffinic hydrocarbons) and the extractant CMPO. GC analyses are accomplished in 20 min using a 15 m × 0.25 μm I.D. DB-5 capillary column with flame ionization detection. The analysis requires derivatization with diazomethane. HPLC analyses are performed in 10 min using a C_{18} reversed-phase column and a mobile phase consisting of acetonitrile–water–triethylamine (79:29.5:0.5) with refractive index and ultraviolet detection. The methods provide information regarding the presence of acidic and neutral impurities in stock extractant, fresh process solvent, and recovered TRUEX solvent.

INTRODUCTION

The TRUEX process[1] is an actinide extraction/recovery process designed to reduce the concentration of the transuranic elements in nuclear waste solutions. The process ultilizes the extractant *n*-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO, **1**, iBu = isobutyl; Ph = phenyl] with tributylphosphate (TBP, **2**) in either a chlorocarbon diluent (tetrachloroethylene) or a normal paraffinic hydrocarbon (dodecane)[2].
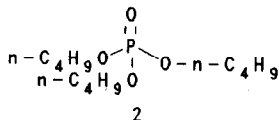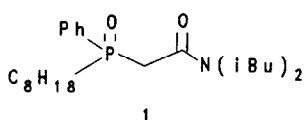
Before the process can be successfully implemented in the reduction of nuclear waste solutions two major technical problems have to be overcome: (1) the commercial production of solvent extraction (SX) grade CMPO and (2) the development of satisfactory analytical methods for determining the purity of extractant and process solvent before and after processing.

A number of impurities are present in CMPO when the extractant is prepared by the Grignard method as developed at Argonne. Horwitz and Gatrone[3] have established a set of criteria for an acceptable purity of the now commercially available extractant. The specifications determined for the SX-grade CMPO are based upon a knowledge of the chemistry of americium(III), the most difficult transuranic metal ion to extract from nuclear waste, in the TRUEX process and the impurities present in the extractant[4,5] which adversely affect this chemistry. The presence of even trace amounts of acidic impurities hampers the back extraction of Am(III) by dilute nitric acid. Because of the complexity of the TRUEX chemistry, a two-tier set of specifications have been developed[a]. The first set of specifications are based on the chromatographic details described in this paper: > 95% (w/w) CMPO, < 2% (w/w) additional neutral organophosphorus compounds and < 3% (w/w) hexadecane. The second set of specifications are based on the performance of the process solvent and will not be described in this paper.

Several acidic and neutral degradation products have been observed due to hydrolysis and radiolysis of the process solvent[6–8]. Any satisfactory analytical technique developed for the analysis of the extractant or fresh process solvent should ideally be applicable to the determination of the continued usefulness of spent solvent and should allow the facile analysis of the process solvent during waste processing. To date, no entirely satisfactory method for the analysis of the TRUEX process solvent or of the extractant has been reported. The development of a capillary gas chromatographic (GC) method for the determination of the concentration of CMPO and TBP in the process solvent has been reported[9], but no attempt to examine the process solvent or commercially available CMPO for the presence of acidic or neutral impurities was made.

The objective of this paper is to report the experimental details of a capillary GC method and a complementary high-performance liquid chromatographic (HPLC) method for the analysis of the TRUEX process solvent. The methods are applicable to fresh and spent solvent and may be applied during the processing of nuclear waste by TRUEX.

EXPERIMENTAL

Technical-grade (95%) CMPO was obtained from M & T Chemical Co. (Rahway, NJ, U.S.A.) and was purified as previously reported[4]. TBP was obtained from Eastman and was distilled from calcium hybride at reduced pressure. Tetrachloroethylene (Gold Label, TCE), Diazald®, anhydrous ethyl ether and triethylamine were obtained from Aldrich and used as received. Methylene chloride (Aldrich) was

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[a] Performance specifications and the data that established these criteria are available from E. P. Horwitz, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, U.S.A.

made acid free prior to use by filtering through a column of alumina. High-purity acetonitrile and water were obtained from Burdick and Jackson and was used after Millipore (0.45 μm) filtration. The potential acidic and neutral impurities: diphenyl-phosphinic acid (DΦP), n-octyl(phenyl)phosphinic acid [OΦP], di-n-octylphosphinic acid (DOP), diphenylphosphine oxide (DΦPO), n-octyl(phenyl)phosphine oxide [O(Φ)PO], di-n-octylphosphine oxide (DOPO), diphenyl-N,N-diisobutylcarbamoyl-methylphosphine oxide [DΦD(iB)CMPO] and di-n-octyl-N,N-diisobutylcarbamoyl-methylphosphine oxide [DOD(iB)CMPO] were prepared as previously described[4,5]. The neutral degradation product from the radiolysis of CMPO, methyl(octyl)-(phen-yl)phosphine oxide [M(O)(Φ)PO], was prepared according to the method of Kaplan as described in ref. 6.

GC analyses

GC analyses were performed on a Hewlett-Packard 5890 (Palo Alto, CA, U.S.A.) equipped with a flame ionization detector, a split–splitless injector and a Hewlett-Packard 3393A computing integrator. A fused-silica bonded-phase capillary column, DB-5 (J&W Scientific, Rancho-Cordova, CA, U.S.A.), 15 m $\times$ 0.25 mm I.D. (0.25 μm film thickness) was employed. The temperature profile was 100°C for 1 min, increased to 260°C at 10°C/min and held for 9 min. The detector and injector temperatures were held at 300°C. Injections of 1 μl were made using a split ratio of 35:1.

Samples were derivatized with diazomethane (CH$_2$N$_2$) to convert any acidic impurities to the respective methyl esters for GC analysis by reaction of an ether solution of the analyte with a freshly distilled ethereal solution of diazomethane at room temperature. The ethereal solution was slowly introduced until the yellow color indicative of excess diazomethane persists. Diazomethane was prepared by the base decomposition of Diazald[10]. The excess diazomethane and ether solvent are removed by gently warming in a water bath until a sample of constant weight is obtained TRUEX samples were prepared by diluting 1 ml of the process solvent (0.25 *M* CMPO, 0.75 *M* TBP in TCE) after derivatization to 20 ml with acid-free methylene chloride. Samples of CMPO were prepared by derivatizing 100 mg of CMPO in ether, followed by the addition of 1 ml of methylene chloride and further dilution to 10 ml.

HPLC analyses

HPLC analyses were performed on a Waters Associates (Milford, MA, U.S.A.) liquid chromatograph equipped with a multisolvent delivery pump (Model 600) and a differential refractive index (RI) detector (Model 410) with a sensitivity setting of 64. Helium sparging of the mobile phase reservoir reduced baseline drift. A program-mable multi-wavelength UV–VIS detector (Model 490) set to 262 nm (0.05 a.u.f.s.) was coupled to the system.
A Waters reversed-phase μBondapak stainless-steel column (30 cm $\times$ 3.9 mm I.D.) was maintained at 32°C. A Waters Model UK6 injector system was used to introduce samples.

RESULTS AND DISCUSSION

GC Analyses

Fig. 1 displays sequential injections of the TRUEX process solvent formulated from purified CMPO and TBP in TCE. Fig. 2 displays the capillary gas chromatogram for a synthetic mixture of potential impurities as well as several structurally similar extractants. The retention times and detectability limits are summarized in Table I.

Previous studies of the GC behavior of CMPO and TBP samples have indicated that these compounds demonstrate linear behavior with respect to a flame ionization detector over the concentration ranges 0.08–0.48 mg and 0.2–1.2 mg[7–9]. The relative behavior of CMPO and TBP are similar such that no internal standard is necessary for the quantitative analysis of the TRUEX process solvent.

However, we are also concerned with the analysis of degraded TRUEX process solvent. Therefore, dibutylphosphoric acid and *n*-octyl(phenyl)phosphinic acid, acidic degradation products from TBP and CMPO, respectively, were selected to calibrate the flame ionization detector for acidic components. The methyl esters of the acidic compounds were prepared by reaction with excess diazomethane. The calibration curves were obtained in triplicate and displayed linear behavior over the range 25–500 ng, the expected range for the impurities to be present based upon the earlier degradation studies[7]. Capillary GC provides a relatively rapid (20 min), reliable method for the analysis of samples of the TRUEX process solvent and its component parts. We have been able to reproducibly detect trace quantities (*ca.* 20 μg) of a variety of structurally similar compounds in the presence of large quantities of the substrates (CMPO and TBP). The data obtained from this method are extremely useful for the analysis of commercial preparations of CMPO for partial specification compliance as well as for the investigation into the hydrolytic and radiolytic stability of the process solvent.

A major limitation of the capillary GC method is the necessity to derivatize the acidic components in order to detect their presence. The free acid forms of the impurities are retained by the column indefinitely and lead to the significant degradation of column performance.
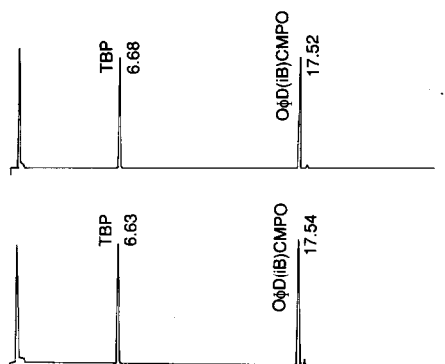

Fig. 1. Replicate injections of TRUEX process solvent. Numbers at peaks indicate retention times in min.
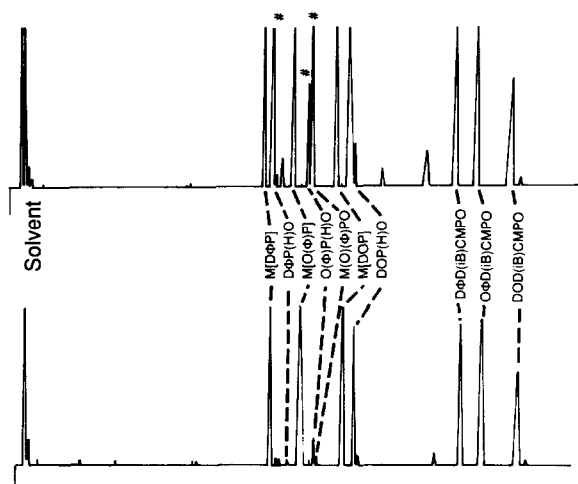
Fig. 2. Injection of the synthetic mixture of impurities and structurally related derivatives. Peaks marked with # were added to the initial mixture after derivatization with diazomethane.

TABLE I

RETENTION TIME AND DETECTION LIMITS FOR POTENTIAL IMPURITIES IN CMPO PREPARATIONS OR TRUEX SOLVENT

Compound		Gas chromatography		Liquid chromatography[a]		
No.	Abbreviation	t_R (min)	Detection limit (µg)	t_R (min)	RI detection limit (µg)	UV detection limit (µg)
1	CMPO	17.54 ± 0.02	–	9.20	0.038	0.031
2	TBP[b]	6.63 ± 0.05	–	6.81	0.51	–
3	(DΦP)[c]	9.84 ± 0.03	18.5	1.98	0.28	0.12
4	(OΦP)[c]	11.03 ± 0.05	21.3	1.99	0.32	0.28
5	(DOP)[c]	12.65 ± 0.02	23.2	2.02	0.31	20.7
6	DΦPO	10.12 ± 0.03	19.3	3.60	0.88	0.15
7	DOPO	13.12 ± 0.05	18.5	–	–	–
8	OΦPO	11.52 ± 0.02	22.3	5.68	0.36	0.22
9	DΦD(iB)CMPO	17.12 ± 0.02	–	–	–	–
10	DOD(iB)CMPO	19.46 ± 0.03	–	–	–	–
11	MOΦPO	11.72 ± 0.03	21.5	5.50	0.30	0.20
12	DBP[c]	4.01	19.8	–	–	–
13	Dodecane[b]	–	–	4.89	–	–
14	CIBA	–	–	4.78	0.08	0.34
15	TCE[b]	–	–	5.93	0.08	0.34
16	Isopar[b]	–	–	4.27	–	–

[a] Retention times are reported for the RI detector; the UV detector retension times are shorter by 0.2 min.
[b] Can be added to form TRUEX process solvent.
[c] Detected as methyl ester by GC.

A second limitation of the GC method is the presence of the tertiary phosphine oxide, M(O)(Φ)PO (**11**), at a retention time (t_R) of 11.72 min in Fig. 2. This phosphine oxide arises because of the thermolysis of CMPO in the injector port. Identification of the peak at this retention time as the tertiary phosphine oxide was confirmed by the synthesis of an authentic sample. Furthermore, the thermolysis of CMPO at 179°C provided significant amounts ($>30\%$) of M(O)(Φ)PO.

$$C_8H_{17}\underset{Ph}{\overset{O}{\underset{\diagup}{\diagdown}}}P-CH_3$$

$$11$$
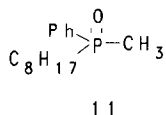
An additional limitation of the GC method is indicated in Fig. 2. It should be noted that only traces of the DΦPO (t_R = 10.12 min) and O(Φ)PO (t_R = 11.52 min) are observed in the lower chromatogram despite the introduction of equal amounts of all impurities prior to derivatization with diazomethane. The retention times of the phenyl-substituted phosphine oxides was confirmed by introducing samples after the derivatization reaction was complete and the excess diazomethane was evaporated. Furthermore, we have observed that DΦPO and O(Φ)PO react with diazomethane to yield the respective methyl esters of the phosphinic acids, *i.e.* diphenylphosphinic acid methyl ester and octyl(phenyl)-phosphinic acid methyl ester (Fig. 3). Secondary phosphine oxides, *i.e.* bis-substituted phosphine oxides with a single P–H bond are tautomeric with the phosphinous acid structure. It is conceivable that the electron-withdrawing phenyl substituent would stabilize the phosphinous acid structure to a degree where a sufficient quantity was present to react with diazomethane yielding the methyl ester of the phosphinous acid. It is well known that the methyl esters of phosphinous acids are very susceptible towards oxidation and rapidly yield the respective phosphinic acid methyl ester upon exposure to air. The hypothesis is further supported by the data in Fig. 2 which indicate that more electron-rich secondary phosphine oxides, such as the dialkylphosphine oxides (*e.g.* DOPO) do not react with diazomethane in this manner.

Another disadvantage of the developed GC method is that repeated injections of underivatized samples of the TRUEX process solvent or of CMPO leads to significant injector contamination, resulting in increased amounts of M(O)(Φ)PO with concomitant loss of quantification. This disadvantage is significantly reduced by derivatizing all samples with diazomethane prior to analysis and a periodic replacement of the injector insert.
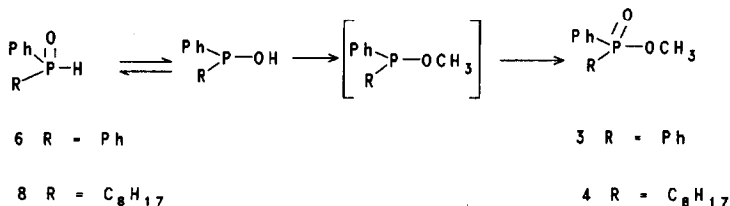
$$\underset{R}{\overset{Ph}{\underset{\diagup}{\diagdown}}}\overset{O}{P}-H \rightleftharpoons \underset{R}{\overset{Ph}{\underset{\diagup}{\diagdown}}}P-OH \rightarrow \left[\underset{R}{\overset{Ph}{\underset{\diagup}{\diagdown}}}P-OCH_3\right] \rightarrow \underset{R}{\overset{Ph}{\underset{\diagup}{\diagdown}}}\overset{O}{P}-OCH_3$$

6   R = Ph   3   R = Ph

8   R = C_8H_{17} 4   R = C_8H_{17}

Fig. 3. The reaction of a phenyl-substituted secondary phosphine oxide with diazomethane.

HPLC analyses

The aforementioned difficulties with the GC method suggested that an alternative, non-destructive analytical technique might have some advantages. HPLC was selected for further evaluation.

Because of the polar nature of the acidic impurities, a reversed-phase column was selected to shorten the analysis time. Various acetonitrile–water mobile phases were investigated for separating CMPO and TBP. The mobile phase ratios were varied from 15 to 30% water, which increased the retention time of CMPO (11 min) and provided baseline separation of the two components. However, the CMPO peak was unsymmetrical with considerable tailing. We were able to resolve these problems by introducing 0.5% triethylamine, which shortened the analysis time to 9 min.

The effect of flow-rate on the separation of CMPO and TBP using acetonitrile–water (70:30) was investigated. Constant flow-rates of 1 and 1.5 ml/min were compared with a programmed flow-rate varied between the two flow-rates. The programmed flow-rate did not significantly enhance the chromatogram with respect to peak shape or tailing reduction compared to the higher flow-rate and also caused baseline drift problems. A flow-rate of 1.5 ml/min decreased the peak width at half-height relative to the 1 ml/min flow-rate, but not enough to justify the extra solvent required. Therefore, the conditions utilized are as indicated in the Experimental.

Two calibration curves were obtained in triplicate for CMPO in the ranges 100–800 mg and 0.1–10 mg or the RI detector. The curves are linear over both ranges with a least squares regression fit of 0.999 for both. A calibration curve for CMPO was obtained in the range 0.1–10 mg for the UV detector with a linear regression fit of 0.999. A calibration curve for TBP in the range 2.72–13.6 mg was likewise obtained for the RI detector and was linear with a fit of 0.994. TBP does not absorb sufficiently for the UV detector to be useful.

The most deleterious impurities to the TRUEX process are the acidic compounds (see above). We investigated the HPLC behavior of DΦP, O(Φ)P and DOP using the optimized analytical conditions. The results are summarized in Table I. The three phosphinic acids elute in appproximately 2 min (Fig. 4) and are unresolved. DOP has a slightly longer retention time but is not baseline resolved. All three compounds were detected using the RI detector. Solvent intereference occurred with the RI detector in the acidic-component retention-time region. To determine if sample volume affected peak height, 0.8 mg of each phosphinic acid was dissolved in 2 and 4 ml of mobile phase and injected. The peak heights were reproducible to within 7% for all compounds and responses were linear over the 0.8–1.6 mg range studied. Despite the lack of peak resolution we were able to obtain a total acidic content for a sample using the RI detector, which was in good agreement with the GC results. For process evaluation, where the exact concentrations of each identifiable acidic component is unnecessary, an analysis of total acidic interference should be sufficient. If further resolution were necessary, a capillary GC analysis could be used.

Only DΦP and O(Φ)P, which contain a chromophore, are detectable using the UV detector. The observed response is linear over the range studied, which is at least twice the detection limit. However, the response factors are quite different, as expected. The stronger chromophore of (DΦP) allows for better UV detection.

Minimum detection limits (signal-to-noise ratio 2) were determined for the three acids and are reported in Table I. For the conditions and instrument settings
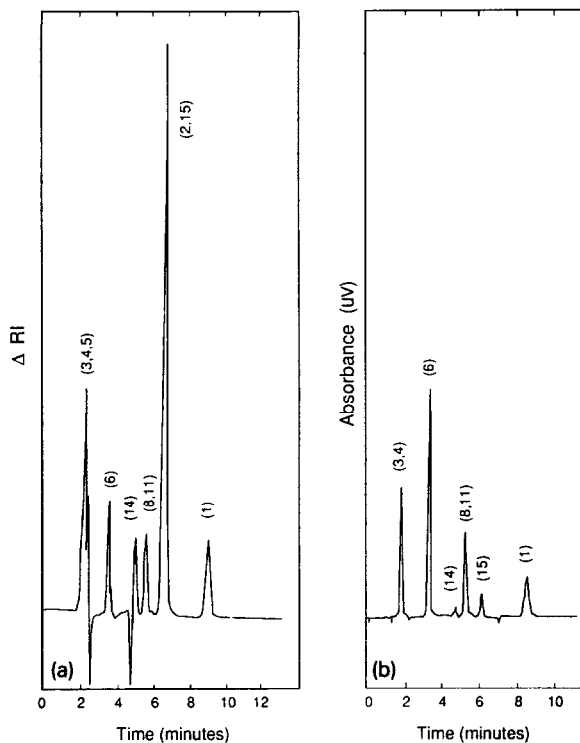
Fig. 4. Detection of a mixture of CMPO (1), TPB (2), (DΦP) (3), [O(Φ)P] (4), DOPO (5), DΦPO (6), O(Φ)PO (8), M(O)(Φ)PO (11), CIBA (14) TCE (15), using RI (a) and UV (b).

indicated, the limits of detection are in a similar range for both detectors. Under these conditions with a 10-μl injection of a 0.2 M solution of CMPO (solubility in the mobile phase is limited to 0.25 M), 0.3 mg (0.04%) of acid impurities could be detected with the RI detector. In the UV detector, a.u.f.s. settings < 0.05 resulted in a noise increase proportional to the signal of the sample. Therefore, to obtain lower detection limits (0.005–0.01 a.u.f.s. working range), an additional noise-reducing filter would need to be installed in the UV–VIS detector.

The UV detector only detected the phenyl-substituted species, whereas the RI detector can detect all compounds potentially present. The RI detector had solvent interference peaks in the acid region, which reduced the detection limits, and the UV detector did not. The detection limits for the UV detector were greater than the RI detector under certain conditions. Using the two detectors in tandem allows one to glean the advantages of both and some speciation may be accomplished.

The neutral impurites or degradation products usually observed in samples of TRUEX process solvent are not generally deleterious to the performance of the process. However, their presence reduces the concentration of the CMPO in the process solvent. In addition, the phosphorus-containing neutral species can degrade or oxidize to acidic impurities.

The neutral secondary phosphine oxide impurities DΦPO, O(Φ)PO, and DOPO have not been observed in degraded process solvent[6] nor are they generally encoun-

tered in commercially available samples of CMPO that we have analyzed. However, M(O)(Φ)PO is formed during the degradation of CMPO by hydrolytic and radiolytic mechanisms[6–8]. It has been suggested that this tertiary phosphine oxide is not significantly deleterious to the process in minor concentrations and may to some extent be able to replace CMPO in the extraction of Am(III) as the CMPO is consumed[6]. However, significant concentrations of M(O)(Φ)PO in the process solvent reduce the overall effectiveness of the process solvent to extract/strip transuranic metal ions and necessitate the replacement of the solvent. Degraded solvent also contains traces of N,N-diisobutylacetamide[7,8]. Commercial samples of CMPO have been observed to contain minor concentrations of 2-chloro-N,N-diisobutylacetamide (CIBA), a starting material used in the preparation of the extractant. Because of the thermal instability of CMPO, which generates M(O)(Φ)PO, and the reaction of phenyl-substituted secondary phosphine oxides with diazomethane (see above), the application of an HPLC method to the neutral impurities also was warranted.

Fig. 4 displays the chromatogram of the acidic impurities [DΦP, O(Φ)P and DOP] and the neutral impurities [DΦPO, O(Φ)PO, M(O)(Φ)PO, CIBA]. The detection limits and retention times are summarized in Table I for both the RI and UV detectors. The compounds fall into three rough regions of the chromatogram with the acidic impurities eluting first, the neutral impurities with TBP and TCE eluting second, and CMPO eluting last. The neutral impurities provide a linear response in the range studied to at least twice their detection limit and provice baseline resolution. The impurities O(Φ)PO and M(O)(Φ)PO are detected by both detectors and could not be discriminated using the HPLC conditions developed herein. Fortunately, these compounds are readily detected by the previously developed GC method. TBP and TCE do not provide baseline resolution under these conditions. However, TCE is detectable by the UV detector and TBP is not, which allows discrimination between the two compounds by use of both detectors. As both compounds are used to formulate the TRUEX process solvent, both would be present in large concentrations and would not interfere with the analysis for CMPO or the impurities.

CONCLUSIONS

The development of a capillary GC and an HPLC procedure for the analysis of TRUEX process solvent provides complementary procedures for the identification and quantification of neutral and acidic impurities in addition to the solvent components. Analyses using the GC method require derivatization before analysis but give reliable identification and quantification data for a diverse number of structurally similar compounds. The development of the complementary HPLC process overcomes some of the difficulties encountered with the GC method. HPLC obviates the need for derivatization, eliminates thermal decomposition during analysis, and readily allows the direct analysis of radioactive process samples. Reliable quantification of total acidic and/or neutral components has been accomplished despite the inability to identify individual acidic or neutral components.

ACKNOWLEDGEMENTS

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