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USE OF GAS CHROMATOGRAPHY IN THE STUDY OF THE OXIDATIVE DECOMPOSITION OF SPENT ORGANIC SOLVENTS FROM REPROCESSING PLANTS

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SUMMARY

A new approach to quantify the oxidizing efficiency of hydrogen peroxide with respect to a complex organic mixture simulating a radioactive organic waste is described, involving capillary gas chromatographic analysis of the reaction mixture with *n*-dodecane as an internal standard.

INTRODUCTION

The solvent extraction systems used in nuclear fuel reprocessing plants for the treatment of irradiated fuels make extensive use of organic extractants[1], and some of the extractants are invariably discarded and treated as secondary radioactive waste. The major problem associated with the management of these wastes is the suitable reduction of their volume, in which all the radioactivity is retained, with a view to less expensive and safer disposal. To date, the methods proposed for the volume reduction of organic radioactive wastes can be divided into dry processes, such as incineration and thermal decomposition, and wet processes, such as acid digestion and related procedures[2].

Recently many papers[3–11] have appeared on wet oxidation methods, describing the use of concentrated aqueous hydrogen peroxide in the presence of a catalyst, especially copper and iron salts, in the oxidation of tributyl phosphate and various kinds of organic substances and diluents used in irradiated nuclear fuel processing.

The processes using hydrogen peroxide–catalyst systems are very convenient for the following main reasons: the process is simple, easy and safe, being managed at atmospheric pressure, at relatively low temperature and under water, and giving rise essentially to water and carbon dioxide; and the off-gases produced are essentially free from radioactivity and also from any dangerous gas (such as NO_x or SO_x).

Currently available papers on the wet oxidation with hydrogen peroxide of organic solvents used as extractants in nuclear fuel reprocessing plants report only that the final products are essentially carbon dioxide and water[3] and prove the effectiveness of the treatment by presenting a non-specific (*i.e.*, cumulative) curve of the residual organic content *versus* the oxidant amount or the parameters of oxidation.

The oxidizing efficiency of hydrogen peroxide towards organic substrates has been occasionally evaluated by total organic carbon (TOC) analysis[4]. However, methods based on TOC analysis are not suitable unless the compounds are completely oxidized to carbon dioxide.

Despite the straightforward nature and the selectivity of chromatographic methods, they are not generally used, probably because of the problems associated with the quantification of the results. In fact, it is not generally too difficult to follow the composition of the organic phase in an organic–aqueous medium (where chemical reactions are proceeding), but the absolute amount of organic phase cannot be exactly determined unless time-consuming procedures are used.

This paper describes the use of capillary gas chromatography (GC) to investigate wet oxidation by 36% (m/v) hydrogen peroxide of a particular simulated (*i.e.*, not radioactive) organic mixture, with a view to volume reduction and safe disposal, and the optimization of the reaction conditions for maximum conversion of the starting organic to inorganic materials.

EXPERIMENTAL

Chemicals

Solvesso 100, a complex mixture composed principally of C_9 (84.5%), C_8 (10.2%) and C_{10} (3%) alkylaromatic hydrocarbons, was supplied by Esso Chemicals (Milan, Italy).

Technical-grade tri-*n*-octylamine containing at least five long-chain tertiary aliphatic amines (TAAs) was supplied by Chemical Procurement (New York, U.S.A.). Mesitylene (1,3,5-trimethylbenzene), tributyl phosphate (TBP) and *n*-dodecane of analytical-reagent-grade were obtained commercially. *n*-Hexane (HPLC grade) and tetrachloroethylene were purchased from E. Merck (Darmstadt, F.R.G.). N,N-Dibutyloctanamide (DBOA) (97%) was obtained from Prochimica (Pavia, Italy), and used without further purification. Hydrogen peroxide (36%) was purchased from Carbo Erba (Milan, Italy). The solid catalysts copper(I) oxide, copper(II) oxide and iron(II) sulphate were also obtained from Carlo Erba.

The reference simulated organic mixture had the following composition: DBOA 30.3, mesitylene 29.5, Solvesso 100 21.2, TBP 4.8, TAAs 3.7 and *n*-dodecane 17.9 volumes.

Apparatus

A Perkin-Elmer Model 8510 gas chromatograph was used, in a version equipped with three detectors (flame ionization, thermal conductivity and nitrogen–phosphorus) and three injectors [a programmed temperature vapourizer (PTV) capillary column injector and two packed column injectors], built-in data handling with re-integration and connected with a Perkin-Elmer GP-100 printer–plotter.

All GC analyses were performed on a Perkin-Elmer BP1 (0.25 μm) column (12 m × 0.22 mm I.D.).

For gas chromatography–mass spectrometry (GC–MS), electron impact mass spectral data were obtained with a Hewlett-Packard quadrupole HP 5970B/5890A instrument with an HP-1 (0.33 μm) capillary column (12 m × 0.22 mm I.D.).

For capillary GC analyses the oven temperature was held at 45°C for 17 min, then programmed at 8°C/min to 300°C and held (3 min).

The PTV injector temperature was set at 300°C 0.01 min after the start of the run and at 0.3 min it was switched off. The septum purge flow-rate was 2 ml/min. The carrier gas was helium at a pressure of 10 p.s.i. and a linear velocity of 30 cm/s. The detector temperature was 330°C, the flame ionization detector attenuation range was $4 \cdot 10^{-11}$ a.u.f.s. and the time constant was 45 ms. The injection volume was 1 μl. Organic samples were diluted 1:11 with hexane (57–60°C from light petroleum). The PTV splitting ratio was 1:100.

Quantitative analyses

In all GC analyses the internal standard method was used with *n*-dodecane as the internal standard (I.S.) and retention times relative to *n*-dodecane being used for identification. Peak-area measurements were used for quantitation.

Wet oxidation

A 250-ml three-necked, round-bottomed flask was equipped with an efficient tap-water reflux condenser with a non-return valve at the top (reaction gases were permitted only to escape). Solid catalyst in an amount ranging from $9 \cdot 10^{-5}$ to $1.44 \cdot 10^{-3}$ mol (ref. 4) was added, followed by 6 ml of the organic mixture.

The reactor was heated at reflux temperature with vigorous magnetic stirring, then 36% hydrogen peroxide was added continuously at a fixed flow-rate, ranging from about 2 to 30 ml/h, with a good-quality peristaltic pump equipped with silicone-rubber tubing. Magnetic stirring was stopped at intervals and samples (a few drops) were removed periodically with the aid of a small I.D. PTFE tube and a syringe, and stored in 1-ml PTFE-faced screw-cap vials.

At the end of the wet oxidation run all the collected samples were diluted with hexane and analysed by capillary GC.

RESULTS AND DISCUSSION

Preliminary runs showed that both copper oxides and iron(II) sulphate are suitable catalysts for the wet oxidation of the reference organic mixture by 36% hydrogen peroxide. However, copper(II) oxide[3] and copper(I) oxide gave irreproducible results whereas iron(II) sulphate did not show effect and was therefore selected as the catalyst for the subsequent study.

Hydrogen peroxide–iron(II) is a well established oxidizing system (Fenton's reagent)[12–14] which acts by means of the production in solution of hydroxyl radicals. It is also well known that secondary reactions lead to hydroperoxy radicals[15], which are much less reactive and promote the unwanted decomposition of hydrogen peroxide to oxygen and water[16]. Hence in wet oxidation processes using metal salt catalysts there is an unwanted but unavoidable production of oxygen. An initial rapid addition of iron(II) to the reaction medium causes a temporary excess, which has been reported to be beneficial in reducing the production of oxygen[16]. Therefore, iron(II) sulphate was introduced at the beginning of the wet oxidation reaction, and the results confirmed the efficiency of this procedure.

Fig. 1 shows the gas chromatogram of a fresh, simulated organic mixture obtained with the oven temperature programmed from 45 to 300°C. All peaks eluting between 3 and 25 min are due to Solvesso 100 components, peaks 1–9 being selected for
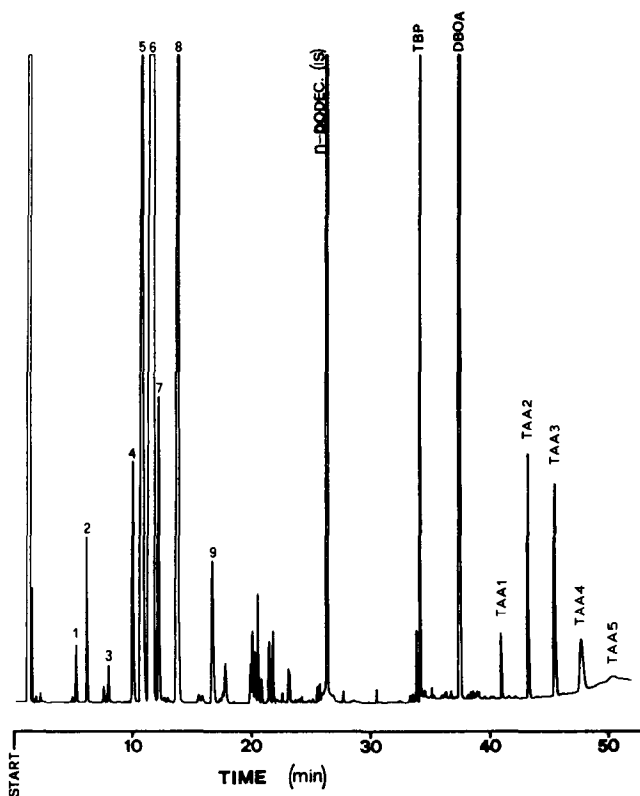
Fig. 1. Gas chromatogram of fresh simulated organic waste diluted 1:11 with hexane. Temperature programmed from 45°C (17 min) to 300°C at 8°C/min. Helium carrier gas, 10 p.s.i. PTV injection of 1 μl with a 1:100 splitting ratio. Linear velocity, 30 cm/s. Flame ionization detector, 4 · 10^{-11} a.u.f.s. Peaks 1–9 relate to Solvesso 100 components; peak 6 is a composite, with mesitylene as the major constituent. Components TAA1–5 were all present in the technical-grade trioctylamine sample.

quantitative evaluation of wet oxidation. Peak 6 corresponds also to mesitylene (see second footnote to Table I). Peaks with retention times below 2 min are due to the hexane used to dilute the original samples.

Fig. 2 shows the gas chromatogram of a wet oxidized organic mixture after reaction with 22 volumes of 36% hydrogen peroxide per volume of fresh organic mixture. In this instance 2.4 · 10^{-4} mol of iron(II) sulphate per millilitre of fresh organic mixture were used. A dramatic change in composition can be seen: all aromatic hydrocarbons were almost eliminated and many very small peaks with retention times ranging from about 27 to about 46 min were observed. Here n-dodecane was more concentrated, because other lipophilic substances disappeared.

These minor peaks appeared gradually after the beginning of the contact with hydrogen peroxide. They are byproducts formed in the oxidative decay of the organic matter. Their height was always very low, indicating that once a low concentration of such intermediates had been established, true conversion to carbon dioxide occurred, a situation resembling a stationary state (i.e., a chemical sequence with the concentrations of the oxidized byproducts remaining almost constant), the net result of which is the conversion of organic substances to carbon dioxide and water.
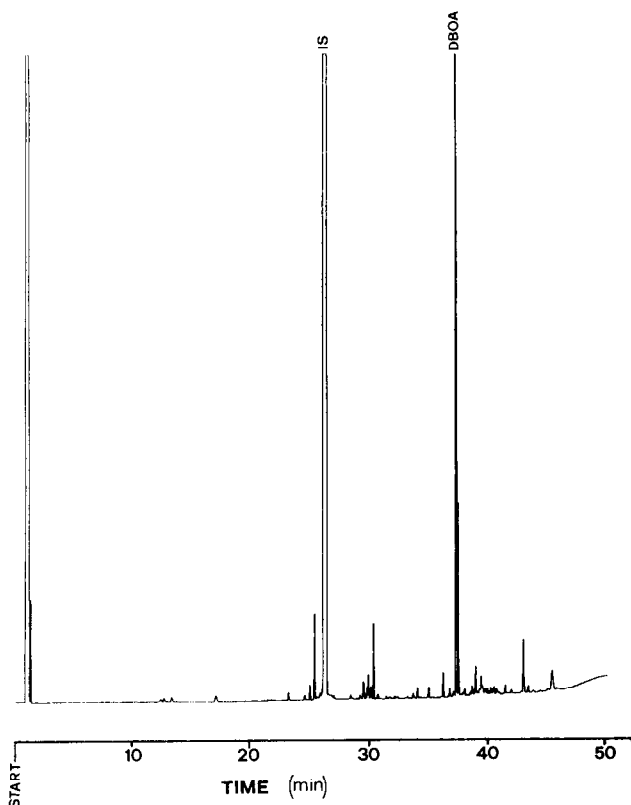
Fig. 2. Organic mixture after addition of 22 volumes of 36% hydrogen peroxide per volume of initial organic mixture [$2.4 \cdot 10^{-4}$ mol of iron(II) sulphate]. Conditions as in Fig. 1.

It should be noted that the oxygen-to-carbon dioxide ratio in the gas phase can be used as an indication of the efficiency of wet oxidation. The variation of this ratio with time can be followed by GC analysis of the off-gases using a system of parallel 2 m × 1/8 in. I.D. packed columns of molecular sieve 5A and Chromosorb 101, both 100–120 mesh, each connected to one side of a thermal conductivity detector[17].

Figs. 3 and 4 illustrate the influence of the amount of catalyst on the oxidative behaviour of all the components of interest in the simulated organic mixture, and Table I reports the GC–MS identification data for the fractions of interest of Solvesso 100 and for the TAAs (for a recent review on the use of GC and GC–MS in the identification of alkylbenzenes, see ref. 18). For clarity, experimental points are reported only for component 1.

As Figs. 3 and 4 show, all aromatic hydrocarbons behave in a very similar manner. A study of the precision of the method described under Experimental gave average relative standard deviations (R.S.D.) below 5% ($n = 3$).

At a constant amount of hydrogen peroxide, the oxidation rate invariably increased with increasing amount of catalyst (from curves a to f). When large amounts of catalyst were used, as in runs e and f, the kinetics showed only minor differences, indicating that larger amounts are impractical.
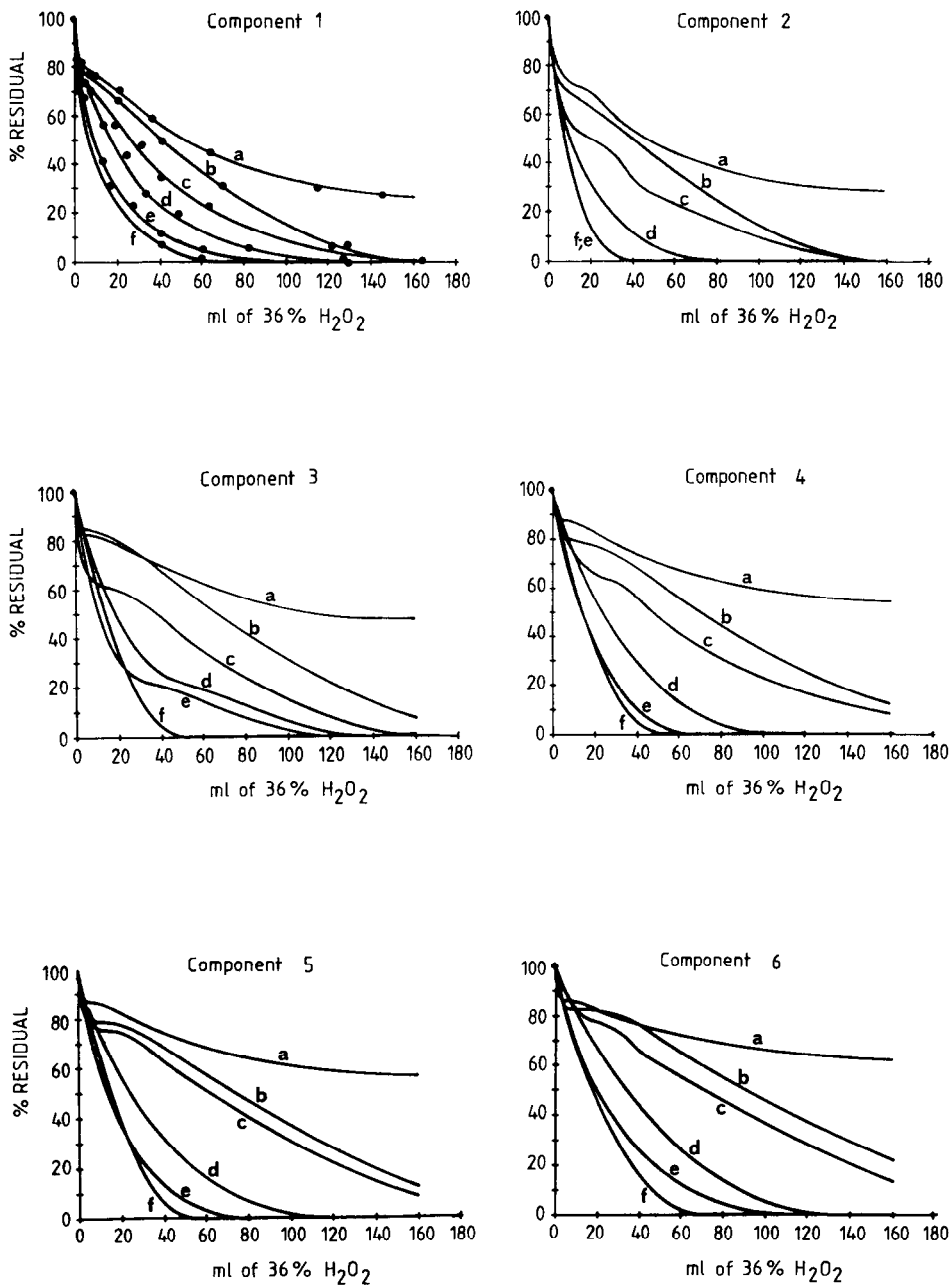
Fig. 3. Residual percentages of components 1–6 (listed in Table I) *versus* volume of 36% hydrogen peroxide Curves a–f relate to runs in wich different amounts of iron(II) catalyst were used: (a) 8.99 · 10⁻⁵ mol (b) = 2(a); (c) = 4(a); (d) = 8(a); (e) = 12(a); (f) = 16(a).
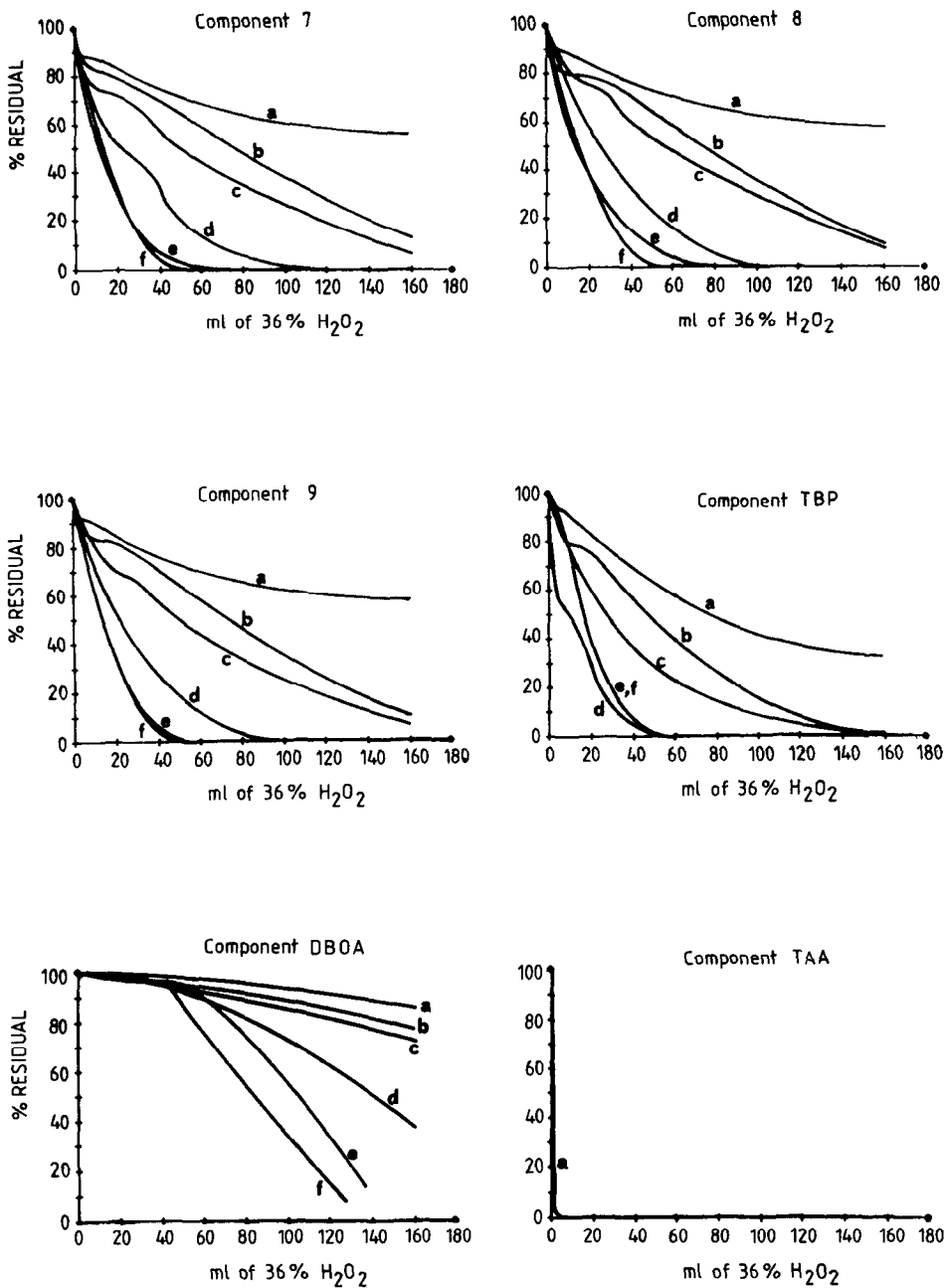
Fig. 4. Residual percentages of components 7, 8 and 9 (Table I), TBP, DBOA and TAAs. Conditions as in Fig. 3. All TAAs reacted very rapidly with concentrated hydrogen peroxide and their concentrations decreased to trace levels until the beginning of the wet oxidation runs. When the differences among runs a–f are not substantial, only run a is shown.

TABLE I

GC–MS IDENTIFICATION DATA FOR THE NUMBERED PEAKS IN FIG. 1

Peak No.	MS-correlation	Correlation factor*
1	1,4-Dimethylbenzene	9813
	1,3-Dimethylbenzene	9795
	1,2-Dimethylbenzene	9737
2	1,2-Dimethylbenzene	9808
	Ethylbenzene	9806
	1,4-Dimethylbenzene	9747
3	1-Ethyl-3-methylbenzene	9739
	1-Ethyl-2-methylbenzene	9685
4	Propylbenzene	9918
5	1-Ethyl-3-methylbenzene	9905
	1-Ethyl-2-methylbenzene	9902
	1-Ethyl-4-methylbenzene	9901
6**	1,3,5-Trimethylbenzene	9842
	1,2,4-Trimethylbenzene	9864
7	1-Ethyl-3-methylbenzene	9904
	1-Ethyl-4-methylbenzene	9899
	1-Ethyl-2-methylbenzene	9871
8	1,2,4-Trimethylbenzene	9853
	1-Ethyl-3-methylbenzene	9834
9	1-Ethyl-3-methylbenzene	9868
	1-Ethyl-4-methylbenzene	9938
TAA1	Triheptylamine	8696
TAA2	Trioctylamine	9971
TAA3	Unknown	
TAA4	Unknown	
TAA5	Not seen with the GC–MS system	

   * A correlation factor of 10 000 means a formally exact MS identification based on the NBS Standard Library.
   ** This is a composite peak in which mesitylene predominates.

It is evident that the reaction rate is highest at the beginning of wet oxidation and is almost independent of the amount of iron(II) salt used. This is confirmed by the fact that, when iron(II) sulphate and organic compounds are mixed, the concentration of iron(II) remains almost constant for a certain time after the start-up of the hydrogen peroxide feed, until the aqueous phase becomes undersaturated with iron(II) owing to the water that is added with the hydrogen peroxide. After a certain time, depending on the initial amount of iron(II) salt and the flow-rate of the peristaltic pump, dilution of the iron(II) really starts, occurring with slower oxidizing kinetics.

The shoulders on the curves in Figs. 3 and 4 may be due to the complexity of the reaction mixture. Oxidized byproducts, formed as intermediates, are more soluble than hydrophobic precursors in the aqueous phase and are probably more easily attacked by concentrated hydrogen peroxide. In the initial stage of wet oxidation, the concentration of these byproducts increases and a substantial proportion of reactive oxidizing radicals is captured by them. When the concentration of intermediates reaches a maximum, the overall rate of wet oxidation is at a minimum, and subsequently the curves show a normal exponential decay due to hydrogen peroxide and catalyst dilution.

The same happens with TBP, whose decay curves closely resemble those of the aromatic components. TBP decomposes to carbon dioxide, inorganic phosphate and phosphoric acid, whereas DBOA is decomposed especially in the final stage of the oxidation run, presumably owing to the gradual decrease in pH that occurs when hydrogen peroxide oxidation takes place. Hence it appears that DBOA is more sensitive to acid hydrolysis than hydrogen peroxide oxidation. Wet combustion of hydrolytic byproducts of DBOA probably proceeds faster, owing to an increased solubility in the aqueous medium of octanoic acid and dibutylamine; these are not observed by GC.

All the TAAs show a very high reactivity with concentrated hydrogen peroxide and no amine peaks are detected by GC even when only a small volume of 36% hydrogen peroxide is added to the reaction vessel. Indeed, it has been known for a long time that tertiary amines react with peracids or concentrated hydrogen peroxide to give N-oxides, which are easily decomposed to alkenes by gently heating (Cope elimination of tertiary amine N-oxides[19,20]).

Fig. 5 shows the effectiveness of wet oxidation with 36% hydrogen peroxide with respect to some of the most significant organic components of the simulated waste as a function of the volumetric flow-rate of addition. The delivery rate ranged from (a) 30 ml/h to (d) about 2 ml/h; the slower the pumping flow-rate of the peroxide, the more efficient is the oxidation.

Particular mention should be made of the behaviour of n-dodecane, whose inertness towards 36% hydrogen peroxide, in the presence of different metallic catalysts and even under reflux conditions, is considered to be remarkable. This result contrasts with the postulated oxidation of n-dodecane to carbon dioxide[3].

Detailed experiments on this n-alkane (Table II) showed that its amount, evaluated by the external standard method, decreased linearly only by ca. 10% after 1 week under wet oxidation conditions. This result suggests that there were exclusively diffusive leaks of n-dodecane to the exterior, mainly with the off-gases, and that no appreciable reactions took place with concentrated hydrogen peroxide. The inertness of n-dodecane towards concentrated hydrogen peroxide is due to its negligible solubility in water and its molecular structure, which is uniformly hydrophobic and lacking in reactive sites.

Evidence that alkanes are resistant to 36% hydrogen peroxide was also obtained wet oxidizing a mixture composed of kerosene, tetrachloroethylene and n-dodecane as internal standard. The GC temperature programme (100°C for 3 min then increased to 200°C at 25°C/min) was applied in order to obtain as far as possible a non-resolved system for the kerosene fraction. Cumulative peak areas and a single response factor were applied to the kerosene peaks. Figs. 6 and 7 show that as the composition of kerosene remained almost unchanged, both qualitatively and quantitatively, the kerosene was not attacked by hydrogen peroxide whereas tetrachloroethylene was easily decomposed. The linear trend (Fig. 7) is distinctive for a non-wet-oxidisable system.

The inertness of n-dodecane towards hydrogen peroxide allowed its use as an internal standard and solved the otherwise extremely difficult problem of quantitative GC analyses in non-homogeneous wet oxidation systems.
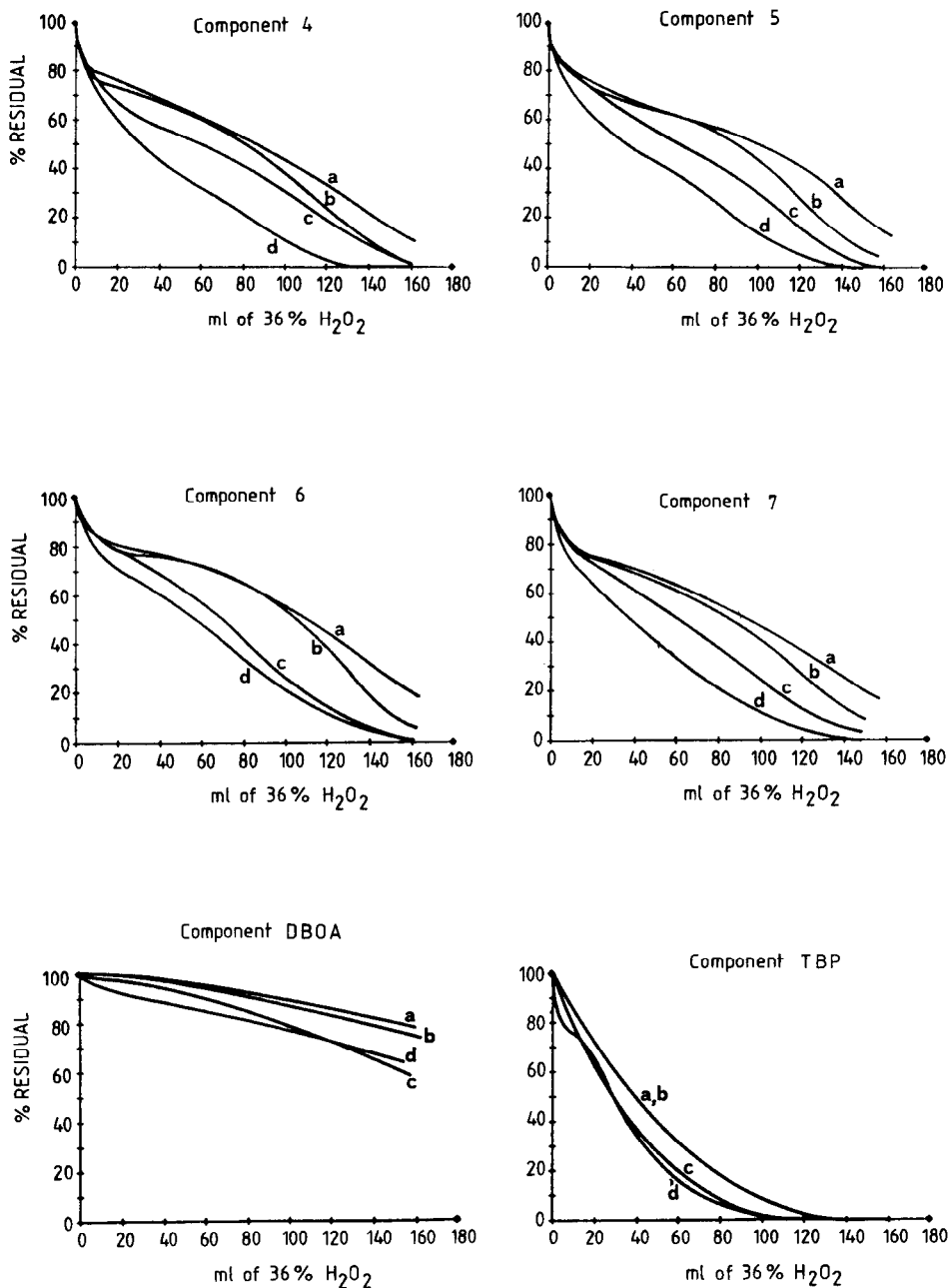
Fig. 5. Influence of the volumetric flow-rate of addition of concentrated hydrogen peroxide: (a) 1.96 ml/h (b) = 3(a); (c) = 10(a); (d) = 15(a). Conditons as in Fig. 1.

TABLE II

CONDITIONS AND RESULTS OF WET OXIDATION RUNS CARRIED OUT TO VERIFY THE INERTNESS OF n-DODECANE TOWARDS HYDROGEN PEROXIDE

Organic mixture	Organic to 36% H_2O_2 ratio (v/v)	Catalyst[*]		Reaction time (h)	Residual (%)[**]	
		Components	Amount (mg)		TBP	n-Dodecane
TBP–n-dodecane (30:70, v/v)	1:20	CuO–Cu$_2$O (50:50)	90	96	0	94[***]
n-Dodecane	1:30	FeSO$_4$ · 7H$_2$O	40	168		91
TBP–n-dodecane (30:70, v/v)	1:20	None[§]		144	40	97
	1:20	Pt–C (1:99, w/w)	90	72	100	93
	1:20	Pt–C (2:98)	45	72	87	98
	1:30	FeCl$_3$	200	72	2	93

   [*] 5 ml of organic mixture reacted.
  [**] Values obtained using the external standard calibration method. R.S.D. = 5 to 7 ($n = 3$).
 [***] Average of two values (R.S.D. > 10).
    [§] Finely emulsified system by the use of 0.5 ml of a concentrated soap builder solution.
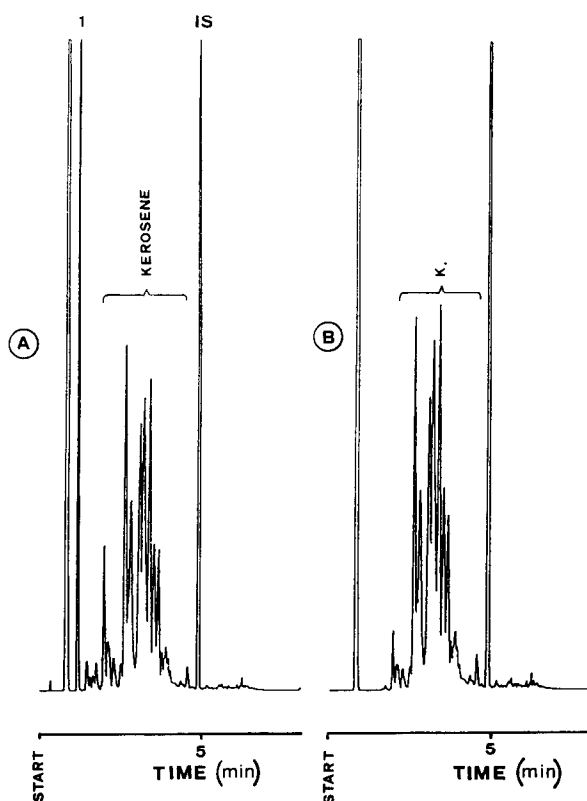

Fig. 6. Wet oxidation run to study the oxidizability of kerosene components and tetrachloroethylene (peak 1). Chromatogram A refers to a fresh mixture composed of hexane (solvent) and tetrachloroethylene–kerosene–dodecane (2:3.2:1) (point A in Fig. 7); B shows the composition of the mixture after addition of 33.3 volumes of a solution of 36% hydrogen peroxide–96% sulphuric acid, (99:1, v/v) (point B in Fig. 7). One volume of organic mixture reacted.
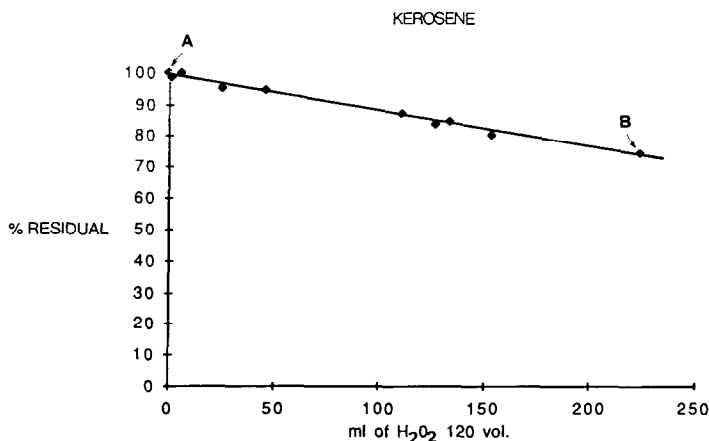
KEROSENE

Fig. 7. Plot of the amount of residual kerosene *versus* the volume of hydrogen peroxide–concentrated sulphuric acid (99:1, v/v). The abscissa represents undiluted (36%) hydrogen peroxide.

CONCLUSION

The concentrated hydrogen peroxide–iron(II) salt system is suitable for the wet oxidation (*i.e.*, wet combustion to carbon dioxide and water) of a simulated organic mixture that reproduces a real radioactive waste coming from an Italian pilot-scale nuclear fuel reprocessing plant.

A quantitative approach has shown that a substantial volume reduction of the waste, composed of alkylaromatic hydrocarbons, TBP, DBOA, long-chain tertiary aliphatic amines and *n*-dodecane, can be achieved, probably with no problems of off-gas radioactivity.

Aromatic hydrocarbons and the alkyl groups of tributyl phosphate and tertiary aliphatic amines are totally and easily decomposed to carbon dioxide and water. Long-chain N,N-dialkylamides such as DBOA show a higher resistance to the oxidative decomposition, but they can also be degraded by wet oxidation in acidic media.

In contrast, *n*-dodecane is not decomposed or attacked by 36% hydrogen peroxide under the conditions used, even in very finely emulsified biphasic systems. At the end of the treatment *n*-dodecane constitutes a very pure alkane phase that can be recovered and reused for other nuclear purposes.

The efficiency of hydrogen peroxide in the wet oxidation depends on the amount of iron(II) sulphate used as the catalyst and also on the rate of addition of hydrogen peroxide to the reactor. Further optimization of these process parameters and a study of the effects of pH and UV light [36% hydrogen peroxide–96% sulphuric acid (99:2, v/v) appears to be very effective] on the wet oxidation process are now in progress. The main objective is the reduction of the excess of hydrogen peroxide needed for quantitative decomposition, with a view to the application of the wet oxidation process to other hazardous non-radioactive organic wastes.

n-Dodecane and homologous compounds can act as suitable internal standards for quantitative capillary GC applied to wet oxidation experiments.

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