

Consolidated Fuel Reprocessing Program

PUREX DILUENT DEGRADATION

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PUREX DILUENT DEGRADATION

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ABSTRACT

The chemical degradation of normal paraffin hydrocarbon (NPH) diluents both in the pure state and mixed with 30% tributyl phosphate (TBP) was investigated in a series of experiments. The results show that degradation of NPH in the TBP-NPH-HNO₃ system is consistent with the active chemical agent being a radical-like nitrogen dioxide (NO₂) molecule, not HNO₃ as such. Spectrophotometric, gas chromatographic, mass spectrographic, and titrimetric methods were used to identify the degradation products, which included alkane nitro and nitrate compounds, alcohols, unsaturated alcohols, nitro alcohols, nitro alkenes, ketones, and carboxylic acids. The degradation rate was found to increase with increases in the HNO₃ concentration and the temperature. The rate was decreased by argon sparging to remove NO₂ and by the addition of butanol, which probably acts as a NO₂ scavenger.

1. INTRODUCTION

The 30% tributyl phosphate (TBP)-70% normal paraffin hydrocarbon (NPH) solvent used in nuclear fuel reprocessing undergoes degradation when contacted with nitric acid and/or intensive ionizing radiation in the first cycle of the solvent extraction process. As a result, both the TBP and the NPH components in the solvent are degraded. The objectives of this investigation were (1) to identify and determine what types of NPH degradation products are formed, (2) to study conditions that promote their formation, and (3) to investigate problems arising from the presence of the different types of degradation products. Although it was not the purpose of the investigation to develop or test a specific solvent cleanup method, the results obtained should be of value, particularly for choosing conditions that will minimize degradation of the NPH solvent.

Solvent degradation has been widely investigated. Blake has provided an excellent review of the early literature,¹ and recent notable investigations include those of M. Nowak² and Z. Nowak et al.³⁻⁵ The degradation products of TBP, principally dibutyl phosphoric acid (HDBP) and monobutyl phosphoric acid (H₂MBP), are known to combine with actinide and fission product ions to form strong complexes which decrease the metal recovery and decontamination efficiencies, and sometimes cause physical problems. These particular degradation products have been extensively studied, and several satisfactory methods^{1,6-8} have been devised to remove them from the solvent before it is recycled. In general, the diluent (NPH) degradation process has not been as well understood as the TBP degradation process and the effects of the diluent degradation products have not been as well defined. Process problems attributed, at least in part, to these degradation products include the formation of emulsions, interfacial "cruds," and precipitates in the process streams. The retention of low levels of fission products in the solvent from one extraction cycle to the next has been attributed to degradation products (e.g., butyl lauryl phosphate) which are thought to be formed in secondary reactions between HDBP or H₂MBP and diluent degradation products and are not removed from the solvent in normal solvent cleanup procedures.

In addition to published data normally referenced in solvent cleanup reports, unrelated literature^{9,10} dealing specifically with the nitration of paraffins and hydrocarbons and similar compounds is particularly relevant to the NPH degradation problem. These important conclusions can be drawn from this information:

1. Nitric acid does not produce an independent chemical effect on the nitration of paraffins but serves solely as a source for the formation and regeneration of nitrogen oxides.
2. The radical-like molecule of monomeric nitrogen dioxide (NO₂) is the primary active chemical agent in this reaction.
3. The initial elementary chemical process in the nitration of a paraffin chain is the formation of organic radicals by interaction with the monomeric NO₂.

It should be noted that the above reaction process is based only on the chemical degradation of paraffins and other hydrocarbons. Historically, a distinction has been made between chemical and radiolytic degradation of TBP-NPH solvents; however, since both radiolytic and chemical degradation proceed through free radical mechanisms, the products obtained may be similar.

2. EXPERIMENTAL METHOD

Solvents consisting of 100% NPH, 30% TBP-70% NPH, or 30% TBP-60% NPH-10% butanol were equilibrated with equal volumes of 2 to 8 M nitric acid (HNO_3) solutions at 25 to 108°C for periods of 1 to 24 h. In most instances, the equilibrating phases were sparged either with air containing 0.5 mol fraction of nitrogen dioxide (NO_2) gas or with 100% argon gas at the rate of 2.5 mL/min per 200 mL of solvent plus aqueous phase.

A schematic diagram of the experimental procedure is shown in Fig. 1. The equilibrations were carried out in all-glass equipment in a flat-bottomed, three-necked boiling flask with an attached water cooled condenser, a thermometer, and a gas sparge tube. A combination magnetic-stirrer and hot plate was used to simultaneously heat and stir the contents of the flask. At the end of each test, the organic and aqueous phases were separated and the organic phase was washed five times with equal volumes of water to remove extracted HNO_3 . A sample of the solvent was taken at this point for analysis, the remainder of the solvent was washed with an equal volume of 0.5 M sodium carbonate (Na_2CO_3) solution to remove HDBP and H_2MBP , and the solvent was again sampled for analysis. The solvent samples, including those not washed with Na_2CO_3 solution, were examined spectrophotometrically using a Perkin Elmer model 575 ultraviolet-visible spectrophotometer and a Perkin Elmer model 283 infrared spectrophotometer. Acid constituents in the solvent samples were determined by potentiometric titration in a water or ethanol medium using a Brinkmann model E536 automatic titrator. Other sample constituents were determined by gas chromatography using a Varian model 3700 chromatograph with a 0.32-cm-diam by 300-cm-long

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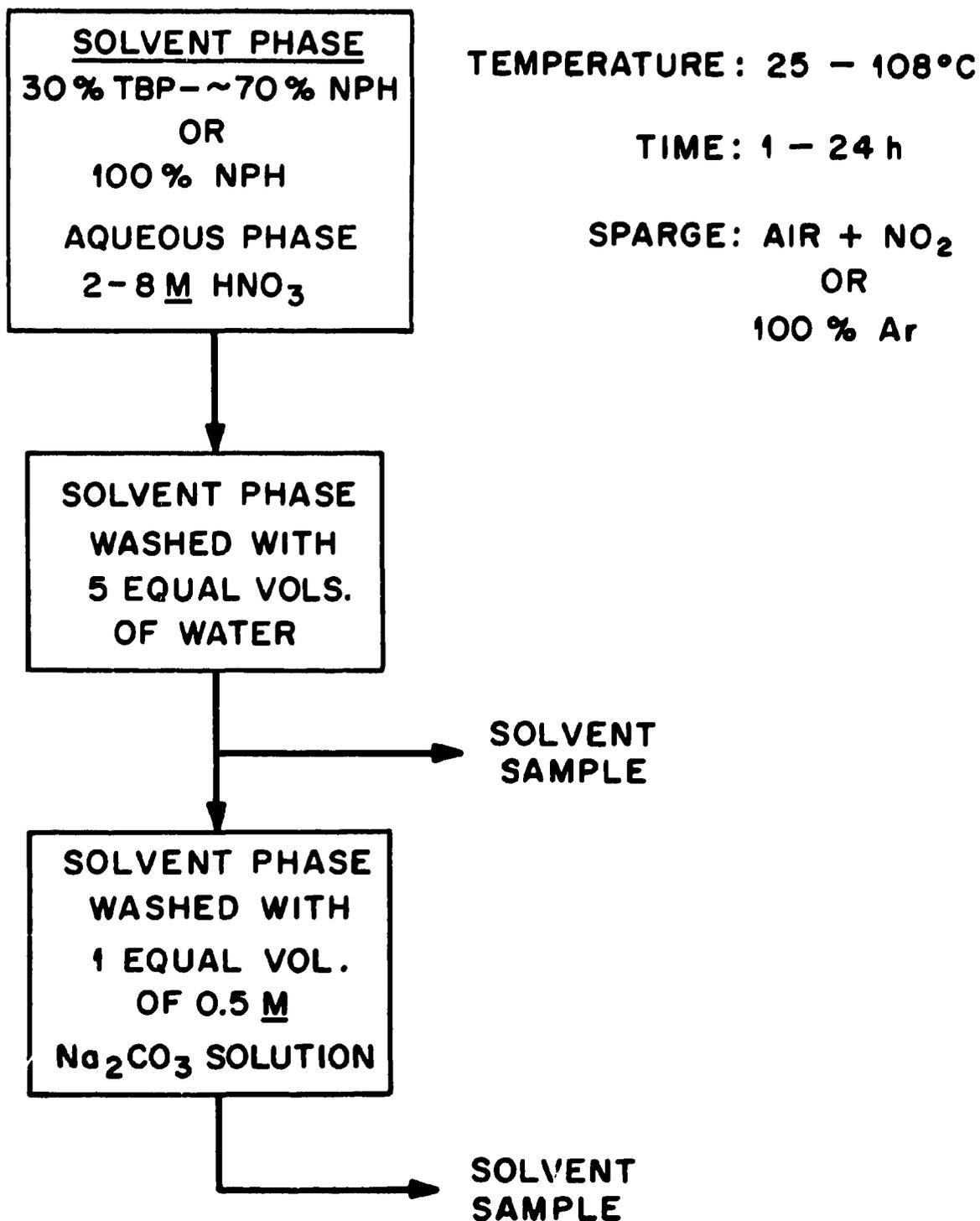


Fig. 1. Outline of experimental procedure.

(1/8-in.-diam by 10-ft-long) column containing 3% Dexsil-400 on 100- to 120-mesh Supelcoport packing. Several samples were additionally analyzed by gas chromatography-mass spectrometry (GC-MS) by the ORNL Analytical Chemistry Division.

The plutonium retention properties (Sect. 3.5) of the washed solvents were determined in various samples by tests in which 5-mL aliquots of the solvent were equilibrated with one drop of 0.17 M Pu^{4+} -1.0 M HNO_3 solution, washed twice with equal volumes of 0.01 M HNO_3 solution, and then sampled for retained gross alpha activity. Phase separation and interfacial tests were also conducted on some of the samples.

3. RESULTS AND DISCUSSION

3.1 NITRO-BEARING DEGRADATION PRODUCTS — NITRO AND NITRATE COMPOUNDS

The initial products formed in the degradation of NPH as indicated in Eq. (2) are nitro and nitrite compounds. The qualitative presence of these compounds in degraded solvents can be detected by spectrophotometric analyses. The infrared spectra of a solvent degraded at $\sim 108^\circ\text{C}$ for 24 h with 8.2 M HNO_3 with an air- NO_2 sparge is shown in Fig. 2. Absorption bands, designated as (a) and (b) in the spectra at 1565 and 1640 cm^{-1} , can be attributed to the presence of nonaromatic nitro ($\text{C}-\text{NO}_2$) and nitrite ($\text{C}-\text{O}-\text{N}=\text{O}$) compounds. Other nitro and nitrite absorptions are covered by normally occurring bands in the infrared spectra of nondegraded 30% TBP-70% NPH. In addition to the nitro and nitrite compounds, the infrared spectra (Fig. 2) indicate the presence of carboxylic acids (peak c).

In other tests, solvents were degraded to a lesser extent to emphasize the appearance of the initial nitro and nitrite degradation products. Near-visible and ultraviolet spectra are shown in Figs. 3 and 4, respectively, for a 30% TBP-70% NPH solvent degraded at $\sim 100^\circ\text{C}$ with 3.8 M HNO_3 with an air- NO_2 sparge for 24 h and then water washed. The near-visible spectra (Fig. 3) exhibit absorption peaks at 334, 340, 357, 370, and 383 nm, corresponding closely to fine structure peaks reported

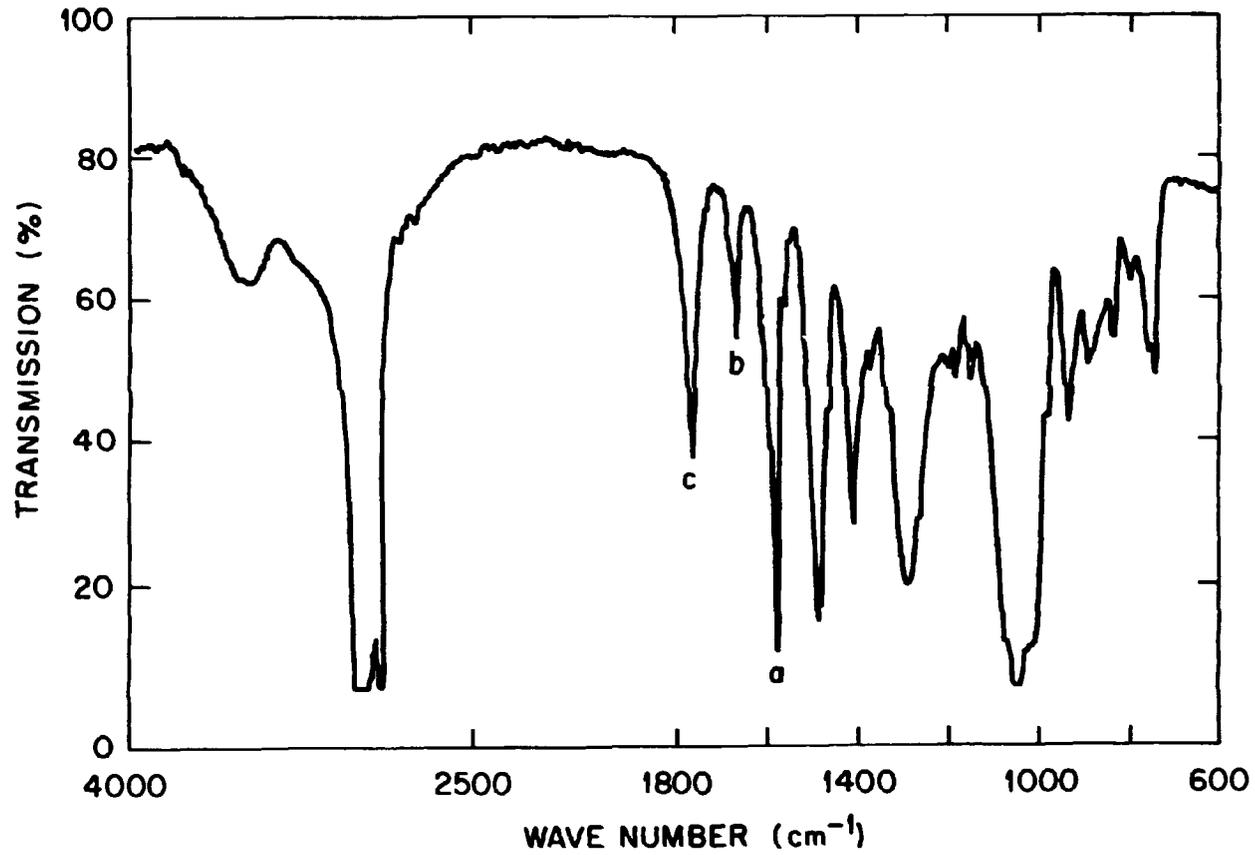


Fig. 2. Infrared spectra of degraded 30% TBP-70% NPH solvent, absorption peaks (a), (b), and (c) not present in non-degraded solvent.

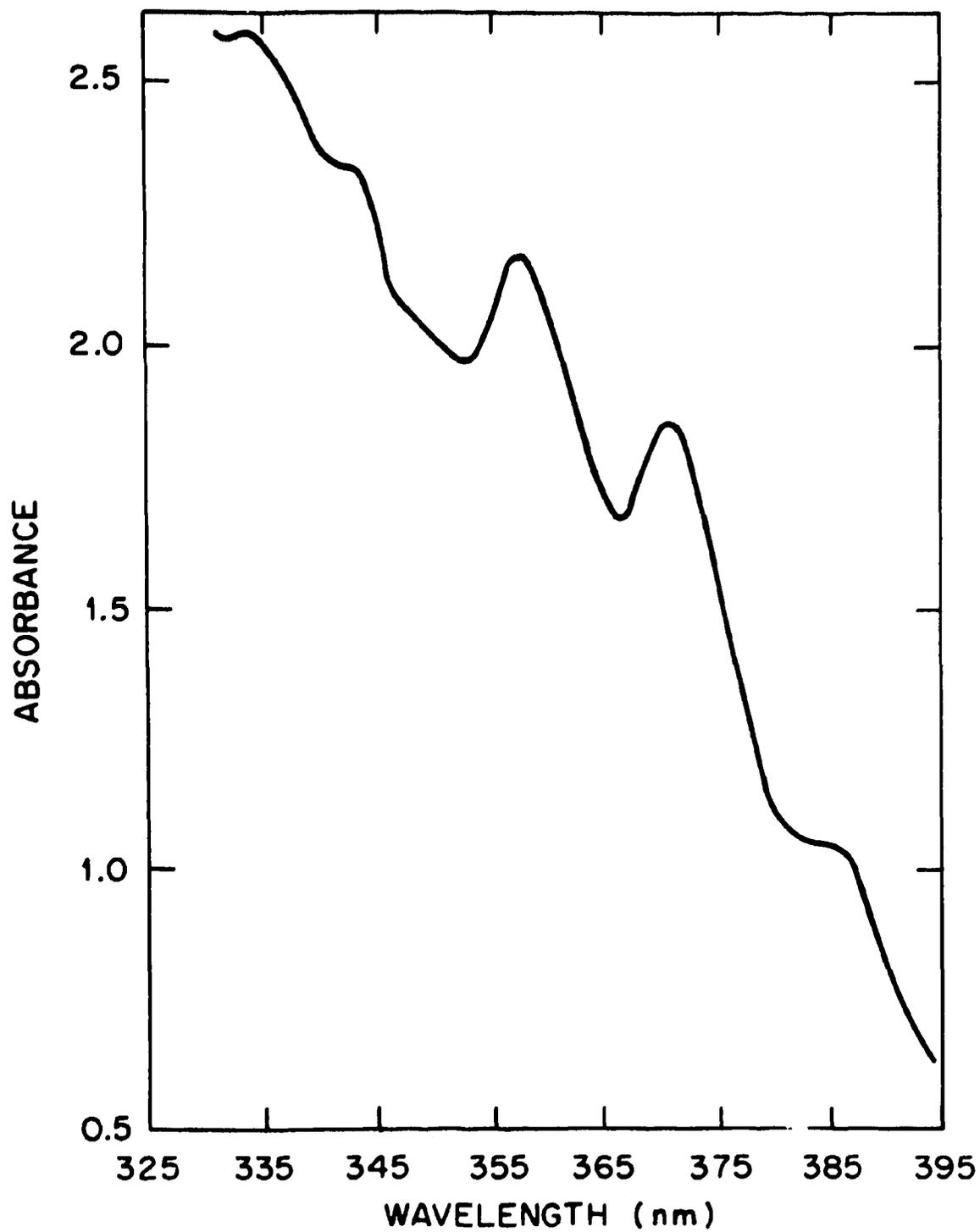


Fig. 3. Visible spectra of degraded 30% TBP-70% NPH solvent.

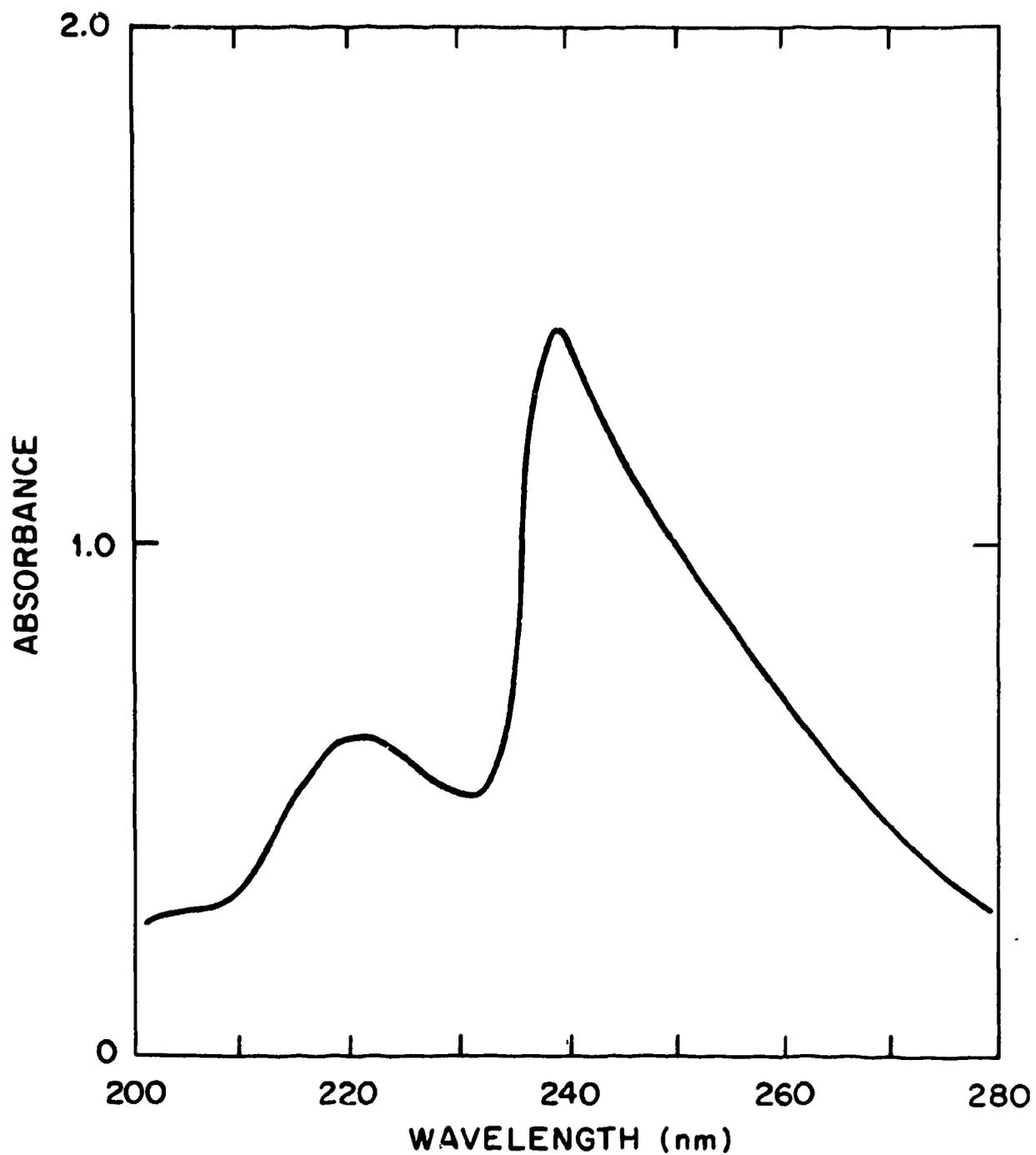


Fig. 4. Ultraviolet spectra of degraded 30% TBP--70% NPH solvent, 1:50 dilution.

for aliphatic nitroso and nitrite compounds.¹¹ The ultraviolet spectra (Fig. 4) exhibit absorption peaks at 223 and 235 nm. Among other compounds, these ultraviolet peaks could indicate the presence of aliphatic nitrites, substituted nitro compounds, or α -nitro alkenes.^{11,12}

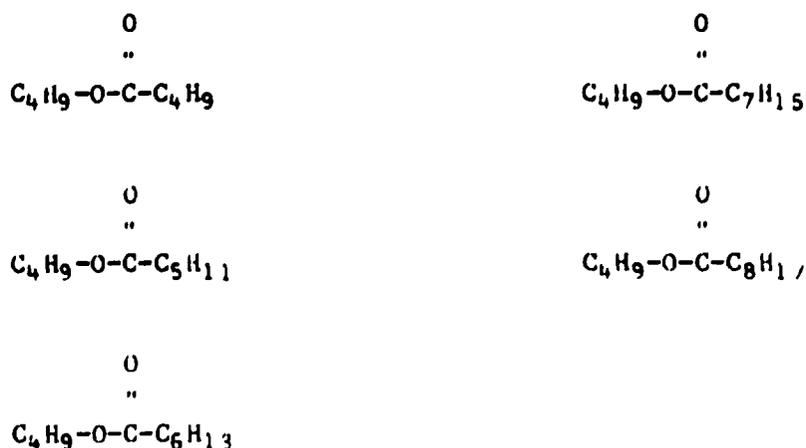
The presence of nitrogen-bearing compounds was also confirmed by GC-MS analyses (see Sect. 3.2).

3.2 GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSES

The most comprehensive view of the overall NPH degradation picture with regard to the quantities and varieties of compounds formed is provided by the GC-MS analyses. A difficult analytical problem is presented by the large variety and small quantities of NPH degradation products formed. The extent to which a number of solvents in this investigation were degraded was at least an order of magnitude greater than would be normally expected in long-term use of fuel recycle process solvents (based on analyses of recycle solvent from the Savannah River Purex Plant). These greater concentrations of the individual degradation products were intended to alleviate the analytical problem. The GC-MS analyses show that the degradation products found when NPH (in the absence of TBP) is degraded to an extent of 10 to 25% are primarily as follows:

1. alcohols,
2. unsaturated alcohols,
3. nitro alcohols,
4. nitro alkenes, and
5. ketones.

The GC-MS technique permits the identification and determination of small quantities of alcohols in the solvent, which cannot be readily analyzed by other methods. The alcohols, to a large extent, are formed by the hydrolysis of alkane nitrites [Eq. (4)], which are the initial NPH degradation products. Table 1 lists the 14 alcohols and isomers that are most commonly detected in degraded NPH solvents. One difference in the degraded NPH and the degraded NPH-TBP solvents is that the latter contain a variety of butyl esters, including the following:



Corresponding esters are also formed from the alcohols or aliphatic acids that are formed by the degradation of NPH. The acids, which are not ordinarily detected by GC-MS analyses, are discussed in Sect. 3.4.

Table 1. Alcohols detected^a in 10 to 25% degraded^b normal paraffin hydrocarbon solvent

| Saturated alcohols | No. of isomers | Unsaturated alcohols | No. of isomers |
|------------------------------------|----------------|------------------------------------|----------------|
| C ₁₂ H ₂₅ OH | 1 | C ₁₂ H ₂₃ OH | 1 |
| C ₁₃ H ₂₇ OH | 3 | C ₁₃ H ₂₅ OH | 2 |
| C ₁₄ H ₂₉ OH | 3 | C ₁₄ H ₂₅ OH | 2 |
| C ₁₅ H ₃₁ OH | 2 | | |

^aBy Varian model 3700 chromatograph with a 0.32-in.-diam by 300-cm-long (1/8-in.-diam by 10-ft-long) column containing 3% Dexsil-400 on 100- to 120-mesh Supelcoport. Temperature range, 110 to 245°C.

^bSolvents degraded by equilibration at 100 to 108°C with 3 to 8 M HNO₃ aqueous solution with air-NO₂ sparge for 24 h.

Figure 5 shows a typical gas chromatogram of a 30% TBP—70% NPH sample for a solvent degraded with 8.0 M HNO_3 at $\sim 108^\circ\text{C}$ for 24 h with an air- NO_2 gas sparge and then water washed. Normally occurring peaks in nondegraded 30% TBP—70% NPH are designated by hash marks in the chromatogram; other peaks indicate the presence of new compounds formed by the degradation process. Calculations of the integrated peak area indicate that the NPH in the solvent was approximately 28% degraded. The molecular weights of the substances in the solvent sample do not show a wide variation; thus, the molar concentrations of the components should be nearly proportional to the peak areas of the chromatogram.

3.3 EFFECTS OF MAJOR VARIABLES

The variables discussed in this section have a significant effect on the rate of degradation of NPH present either in the pure form or mixed with TBP.

3.3.1 Nitric Acid Concentration and Argon Sparge

The degradation of NPH as a function of time when initially pure NPH was contacted with 4.0 and 8.2 M HNO_3 at 101 and 108°C , respectively, is illustrated in Fig. 6. As shown, the degradation is approximately ten times greater with 8.2 M than with 4.0 M HNO_3 . The NPH contacted with 8.0 M HNO_3 was 21.3% degraded in 6.75 h, whereas that contacted with 4.0 M HNO_3 was only 1.6% degraded in 6 h. In each instance, the degradation rate remained approximately constant during the 7-h interval. The effect of aqueous-phase HNO_3 concentration and argon sparging on the degradation, at 101 to 108°C for 24 h, of NPH solvent mixed with 30% TBP is presented in Fig. 7. With an air- NO_2 gas sparge, the amount of degraded NPH increased from $\sim 3.6\%$ in 3.8 M HNO_3 to $\sim 35\%$ in 8.2 M HNO_3 . With an argon sparge, the extent of degradation was significantly restricted to $\sim 0.17\%$ with 3.8 M HNO_3 and to $\sim 1.15\%$ with 8.2 M HNO_3 . As with NPH solvent without TBP, the degradation rate remained approximately constant with time.

There may be partial chemical recycle of the NO_2 and/or HNO_2 , which are the principal reactants in the system. The NO_2 first reacts with a hydrocarbon radical as

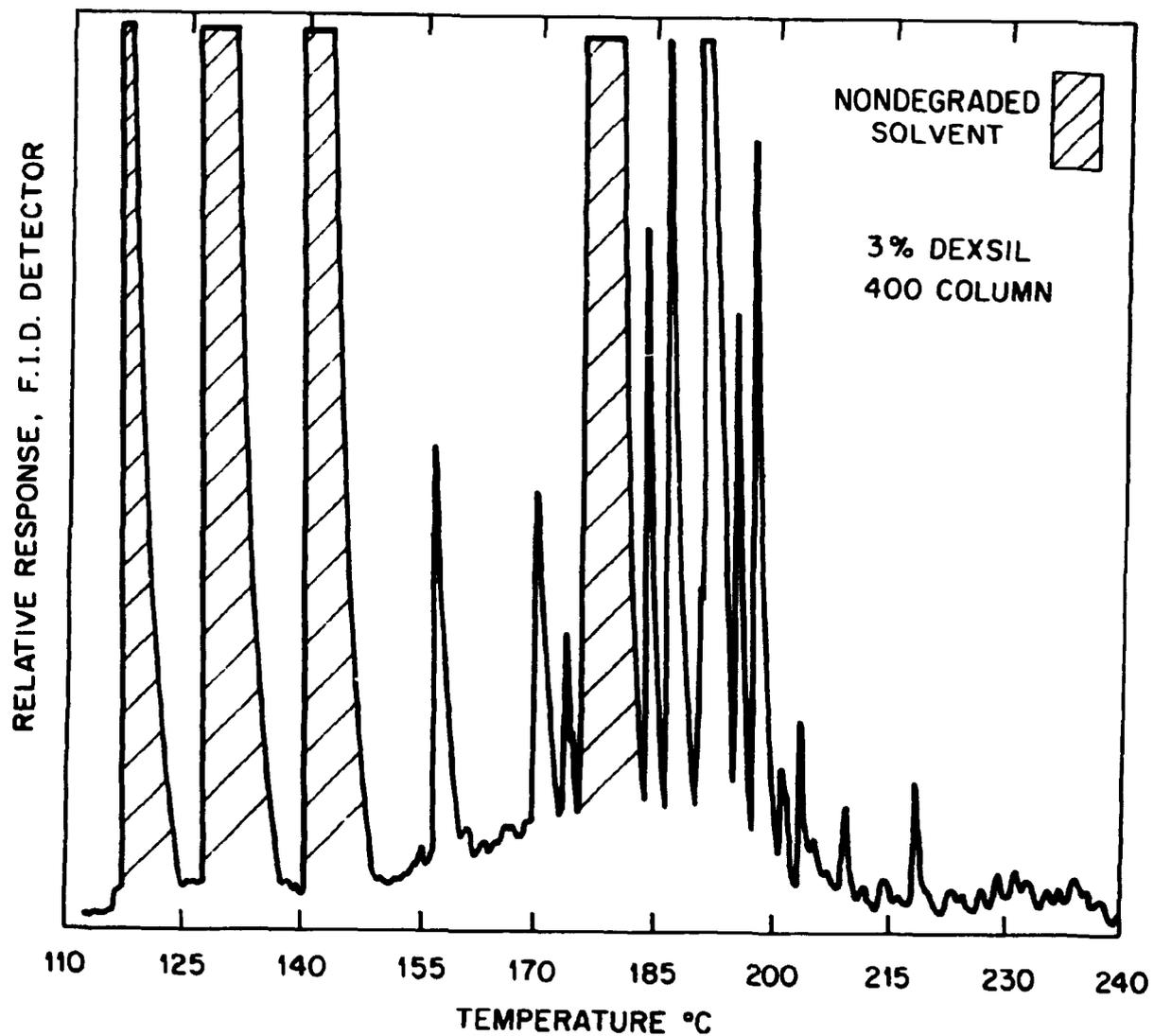


Fig. 5. Gas chromatography of degraded 30% TBP-70% NPH solvent.

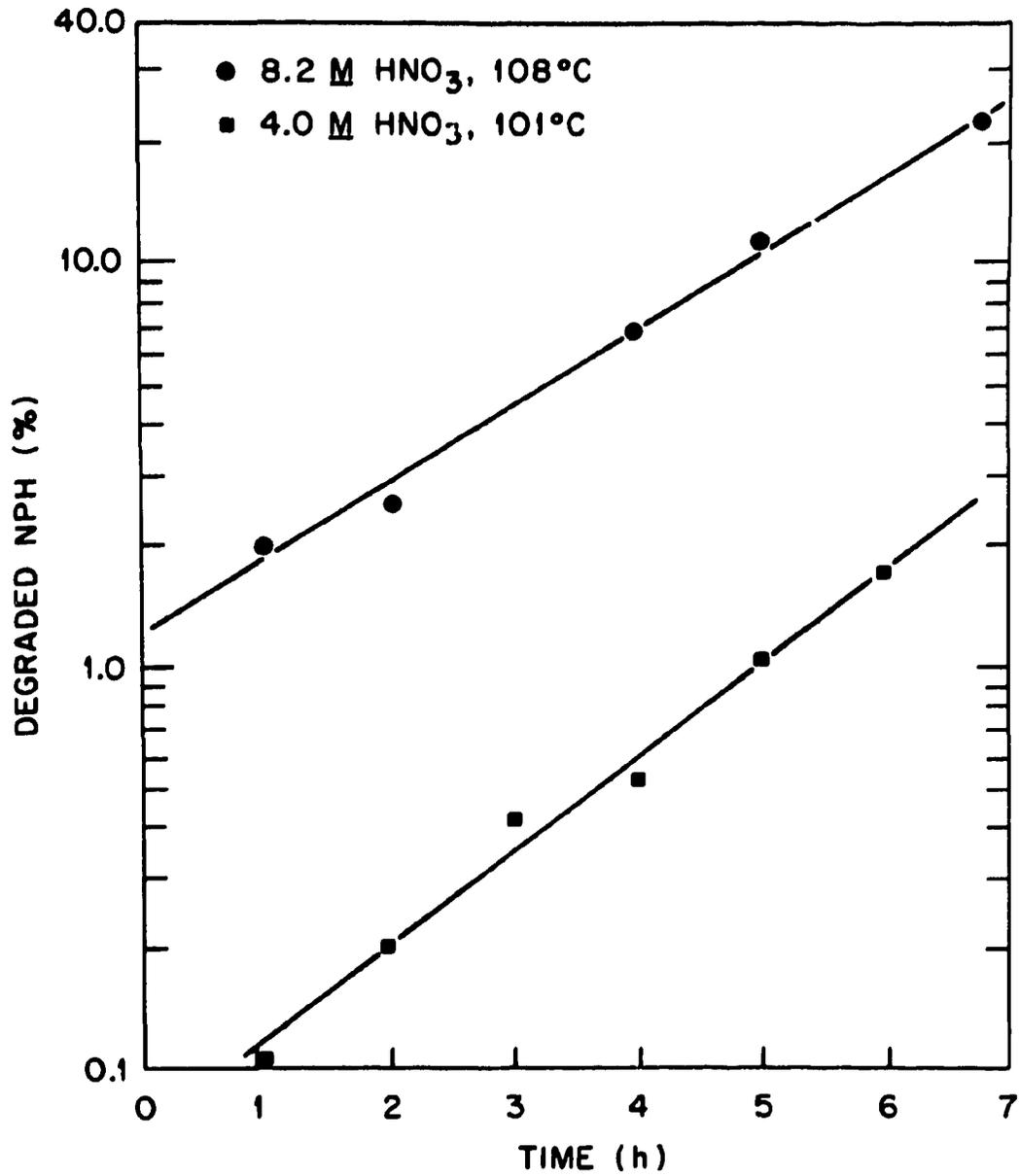


Fig. 6. Degradation of NPH as a function of time with 8.2 and 4.0 M HNO₃ and air-NO₂ sparge at 100 to 108°C.

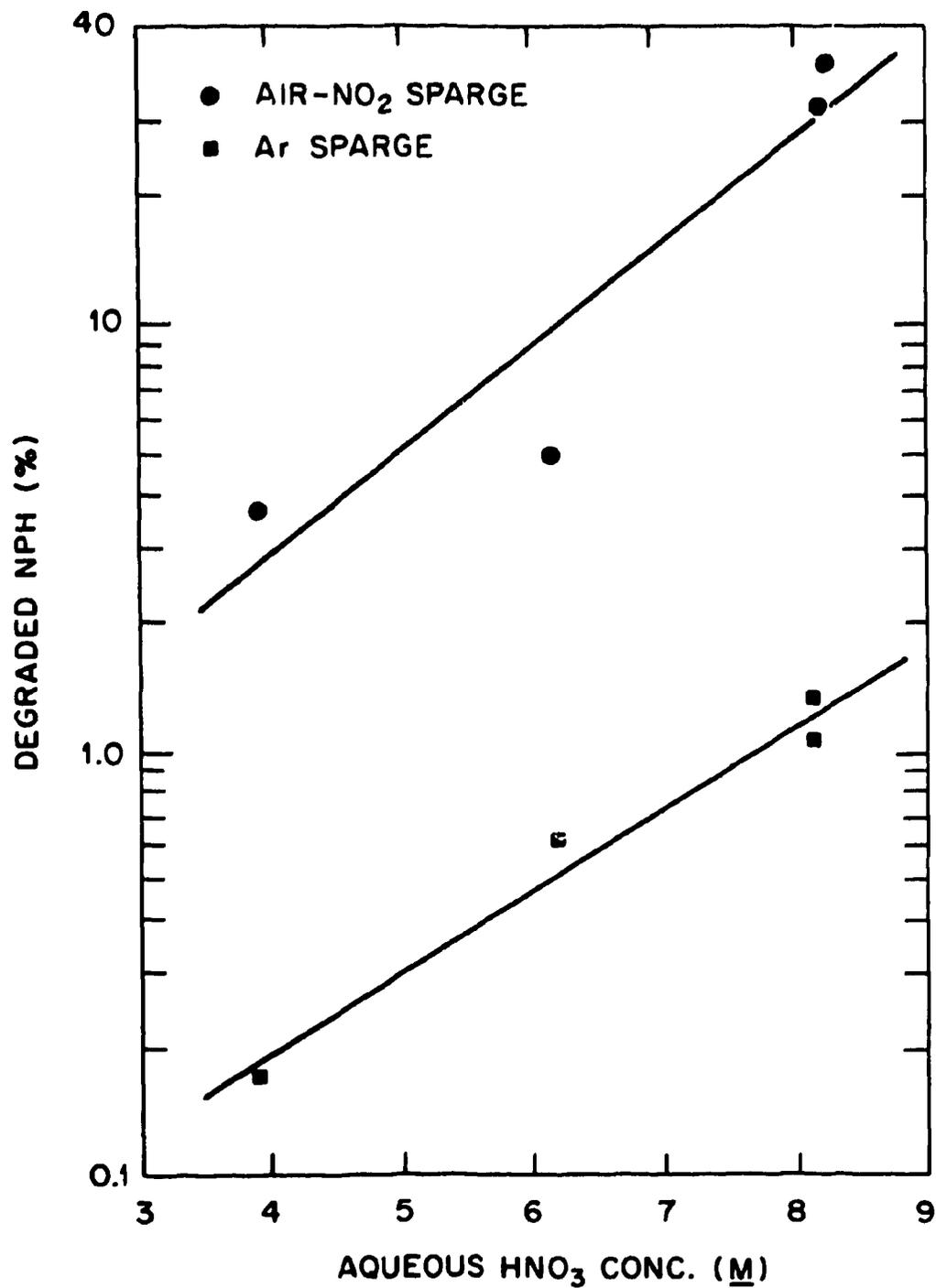
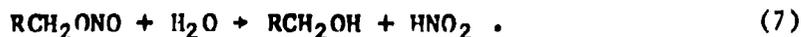


Fig. 7. Degradation of NPH from initial 30% TBP~70% NPH with HNO₃ solution at 100 to 108°C for 24 h.



and then is reformed as HNO_2 by the reaction



These reactions give rise to consumption of reactant (i.e., NPH) and production of NPH degradation products.¹⁰ Additionally, the effect of the argon sparge in decreasing the degradation rate is consistent with NO_2 and/or HNO_2 being the principal reactants. Not only is the NO_2 excluded from the sparge gas, but the NO_2 formed from the HNO_3 tends to be removed from the system. Apparently, the sparging action with either gas sets up a steady-state NO_2 concentration (low in the case of argon gas) such that the degradation rate remains constant with time.

The HNO_3 concentration of the aqueous solution contacted with NPH or TBP-NHP solvents indirectly influences the rate of NPH degradation since the higher aqueous-phase HNO_3 concentration increases the steady-state level of NO_2 and/or HNO_2 .

3.3.2 Butanol Addition

It is apparent from tests conducted with solvents containing 30% TBP-60% NPH-10% $n\text{-CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$ that the butanol [$n\text{-CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$] component blocks the reaction sequence in diluent degradation, perhaps by scavenging NO_2 or HNO_2 in the solvent and thus decreasing the degradation of the NPH. The dramatic effect of the butanol can be seen in gas chromatograms of the degradation products for solvents degraded with and without butanol (see Fig. 8). Each of the solvents had been equilibrated with equal volumes of 8.2 M HNO_3 aqueous solution for 24 h with an air- NO_2 gas sparge and then successively washed with water and Na_2CO_3 . Based on the chromatogram (only partially shown in Fig. 8), the presence of the butanol resulted in a decrease in NPH degradation from ~28% to ~3%. Some reactions of butanol with HNO_2 or NO_2 are possible,

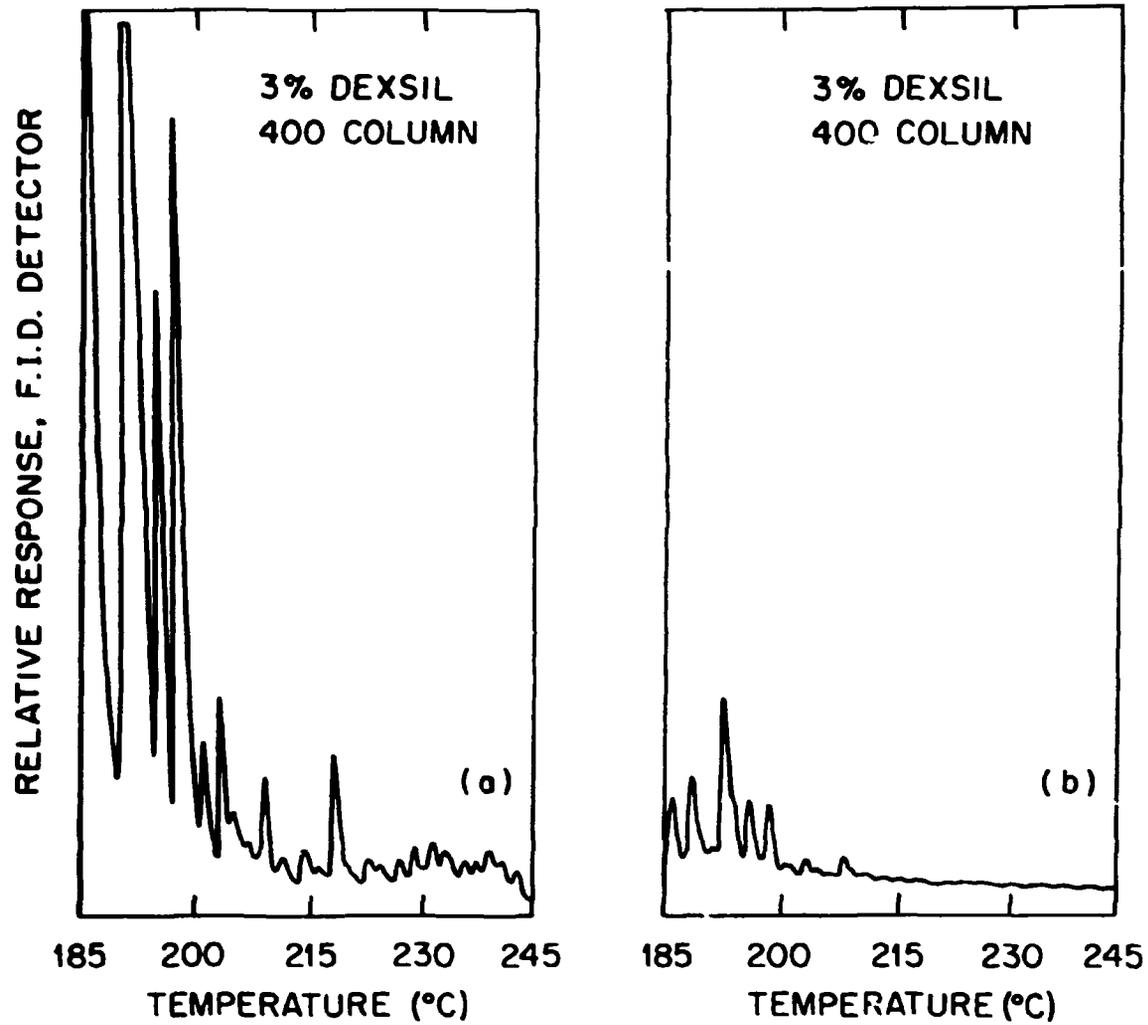


Fig. 8. Gas chromatograms of solvent degradation products produced (a) without added butanol and (b) with 10% added butanol.

but products normally expected from these reactions were not detected in the degraded solvents; however, the analytical methods used for their detection may have been inadequate. A large fraction of the products may have been removed in the washes and/or volatilized from the solvent by the sparge gas.

3.3.3 Temperature

The quantity of NPH degradation products formed at 25°C (all other conditions being equal) is generally an approximate order of magnitude less than the quantity formed at 100 to 108°C. Under the most beneficial conditions (i.e., with a low acid concentration, ~4 M HNO₃, and with an argon sparge), the amounts of degradation products formed in 24 h at 25°C were almost undetectably small.

3.4 LONG-CHAIN ALIPHATIC ACIDS

The long-chain aliphatic acids are relatively stable (other than forming esters) and probably, to a large extent, represent end products in the NPH degradation process. The general reaction by which the acids are formed is shown in Sect. 1 [Eq. (5)].

3.4.1 Titrimetric and Infrared Analyses

The presence of long-chain aliphatic acids in degraded solvents can be detected by potentiometric titration and infrared spectral analyses. A potentiometric titration curve for 1.0 mL of 28% degraded solvent that initially contained 30% TBP-70% NPH is shown in Fig. 9 (a). The titration was carried out with the sample in ethanol medium using an automatic titrator (Sect. 2). The equivalence point with ~0.15 mmol of titrant added [curve (a), Fig. 9] represents the point where dibutyl phosphoric acid, which is a degradation product of the TBP, was titrated. The difference between the equivalence points at ~0.15 and ~0.90 mmol of titrant added represents the concentration of long-chain aliphatic acids (e.g., dodecanoic acid) which were present in the solvent. Titration of a duplicate sample with added dodecanoic acid is shown by curve (b) in the figure. The only effect of the added dodecanoic acid is to shift the equivalence point. The organic acids in

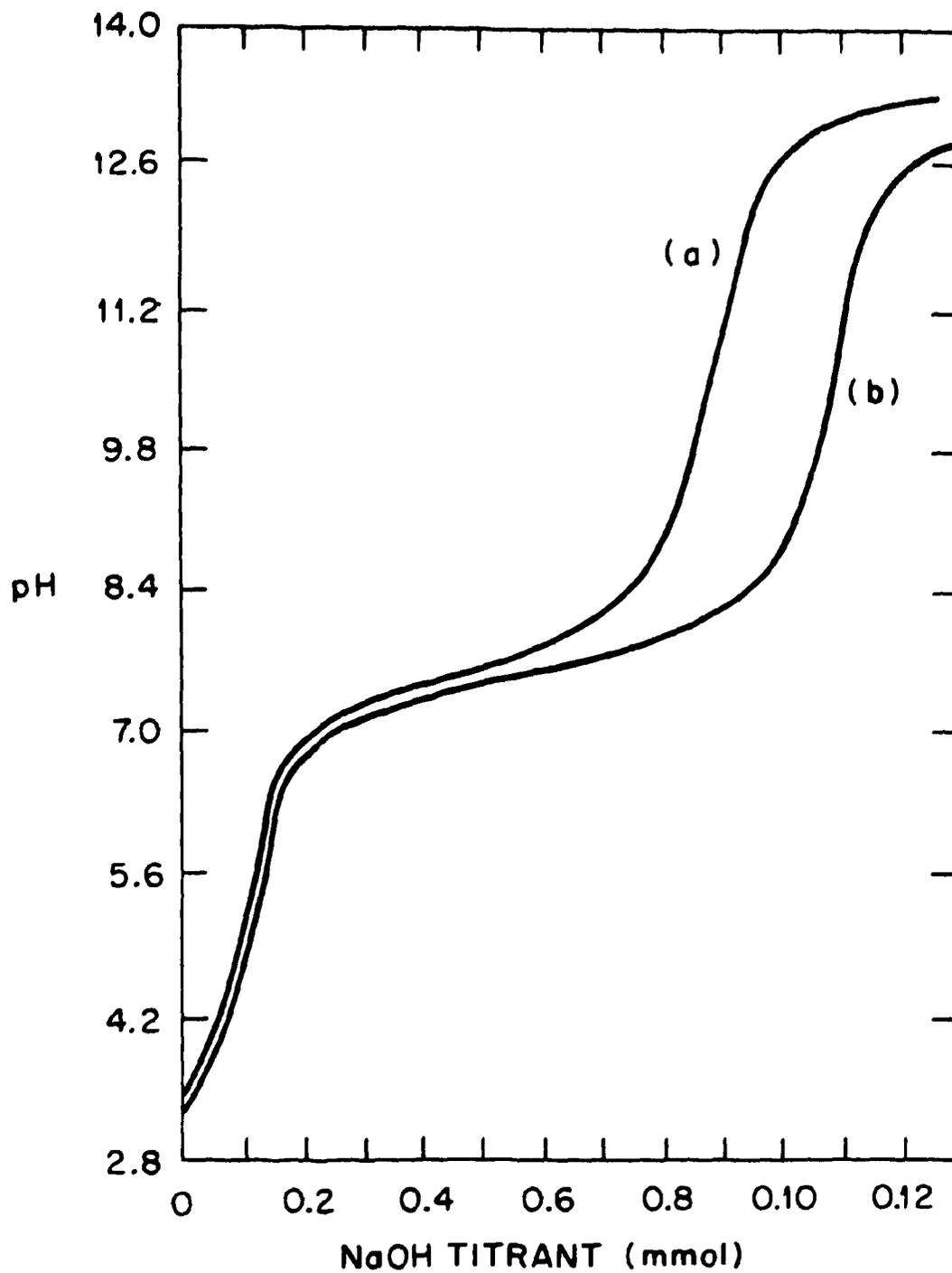


Fig. 9. Titration curves for: (a) 1 mL of degraded 30% TBP~70% NPH; (b) 1 mL of degraded 30% TBP~70% NPH plus 0.2 mmol dodecanoic acid.

degraded solvent samples can be titrated, with some difficulty, in aqueous media instead of ethanol if an automatic titrator is used and the procedure is carried out slowly over a period of ~1.5 h. The organic acids are not fully detected in aqueous media if the titration is carried out rapidly.

The infrared spectra of the 28% degraded solvent are shown in Fig. 2. The peak at $\sim 1750 \text{ cm}^{-1}$ [(c) in the figure] is in the absorption band region of the carbonyl group in carboxylic acids. The infrared spectra further substantiate titration data, showing the presence of the long-chain acids in the degraded solvents. Shorter-chain acids may also have been formed in the degradation process and washed out of the solvent in the sample preparation procedure.

3.4.2 Effects of Aliphatic Acids in the Solvent

Phase separation problems have been reported in the Na_2CO_3 scrubbers used in plant processes to clean up recycle 30% TBP—70% NPH solvents. The long-chain organic acids formed by degradation of the diluent are suspected to be the source of the problem since contact with Na_2CO_3 causes the acids to form sodium salts (soaps). In simulated tests the interfacial tension of the organic phase in contact with 0.5 M Na_2CO_3 was noticeably decreased by sodium laurate concentrations as low as 10^{-4} M (Fig. 10). At concentrations above $\sim 10^{-3}$ M, the interfacial tension dropped precipitously. The figure also shows the effect on the phase separation time in a mixer stirred by a 0.5-in.-diam perforated blade turning at 2400 rpm for 1 min. Note that starting at $\sim 10^{-3}$ M sodium laurate, the organic phase did not completely clarify even though a clear aqueous phase did separate. Above 3.3×10^{-3} M, the phases did not separate in 1 d. We determined the long-chain organic acid content of the Savannah River Plant (SRP) solvent to be ~ 0.0013 M, which is in the region where phase separation problems are imminent. However, SRP solvent shows better phase separation behavior than synthetic degraded solvent with the same long-chain organic acid content, possibly due to the beneficial effects of other degradation products present in the SRP solvent.

Figure 11 shows the distribution of sodium laurate between water and 30% TBP-70% NPH. At sodium concentrations present in standard Na_2CO_3 scrubbers, the distribution to the aqueous phase will be much less favorable than to water; most of the sodium laurate will remain with the organic phase and pass back into the solvent extraction system. It should be possible to continuously remove the sodium salts of the long-chain organic acids by following the Na_2CO_3 scrubber with a water or very dilute Na_2CO_3 scrubber; this may not be feasible with badly degraded organic solvent since an unmanageable emulsion will probably form in the aqueous scrubber. The long-chain organic acids were initially suspected of contributing to metal-ion retention problems, but tests have shown that they do not cause significant retention of either uranium or plutonium. While they do produce changes in the extraction and stripping behavior of UO_2^{2+} and Pu^{4+} , these effects will be negligible in the concentrations expected in a nuclear fuel processing plant.

3.5 PLUTONIUM RETENTION TESTS

Plutonium retention tests were conducted on a number of degraded solvents that had been washed three times with equal volumes of 0.01 M HNO_3 and once with an equal volume of 0.5 M Na_2CO_3 solution. The experimental method used in the retention tests is described in Sect. 2. Since the principal degradation products of TBP (i.e., dibutyl and mono-butyl phosphate)¹³ are removed by the Na_2CO_3 wash, any plutonium present in the solvents is considered to be from NPH and/or secondary TRP degradation products such as butyl lauryl phosphate.

When NPH is degraded ~25%, it exhibits plutonium (Pu^{4+}) retention even when TBP is not present. When it is degraded without a gas sparge, the retention ranges up to $\sim 5 \times 10^{-5}$ M. When the solvent is degraded with an argon sparge, the retention is decreased by a factor of ~100.

The effect of argon sparging on the plutonium retention properties of degraded TBP-NPH solvents (initially 30% TBP-70% NPH) depends on the temperature at which the solvents are degraded. Solvents degraded with 4, 6, and 8 M HNO_3 at 25°C while sparging with argon had plutonium retention values that were 16, 27, and 3%, respectively, of those measured for similar solvents sparged with air- NO_2 mixtures under the

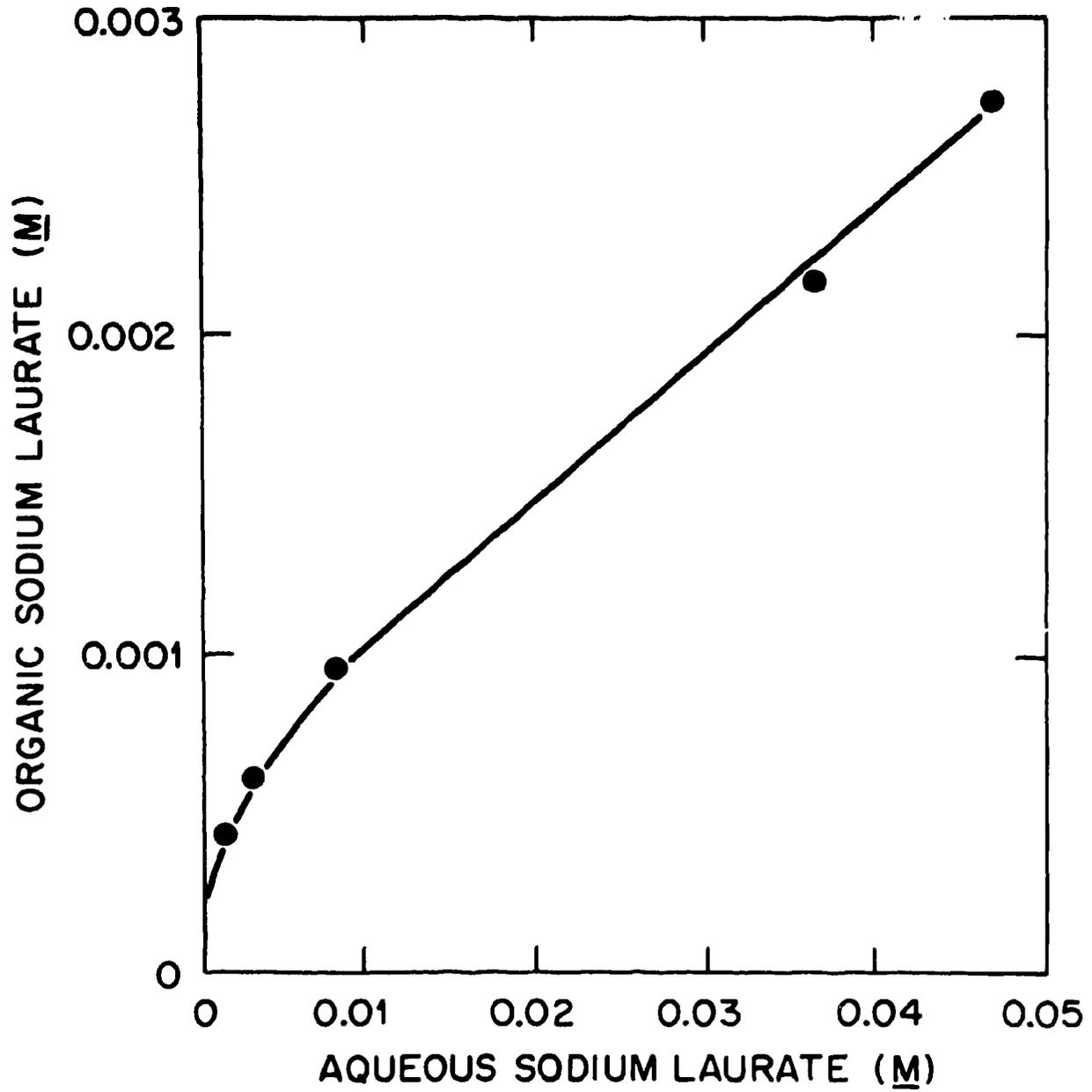


Fig. 11. Extraction of sodium laurate by 30% TBP--70% NPH.

same conditions. However, the argon sparge had no beneficial effect on plutonium retention (5×10^{-5} to 5×10^{-4} M) for solvents degraded at 100°C ; the retention in solvents sparged with either argon or air- NO_2 gas mixtures increased by about two orders of magnitude over that of NO_2 -air sparged solvents degraded at 25°C . Although the argon sparge decreases the total quantity of NPH degradation products formed at 100°C by about an order of magnitude (see Sect. 3.3.1, Fig. 7), those components that are responsible for plutonium retention are apparently not appreciably decreased.

Several general observations can be made with regard to the plutonium retention tests. Even in solvents where the NPH component is an order of magnitude more degraded than would be expected in a plant process, the plutonium retention is low (only $\sim 5 \times 10^{-5}$ to 5×10^{-4} M). If it is assumed that the concentration range of the complexing reagent (degradation product) retaining the plutonium in the organic phase is approximately the same as the retained plutonium in the solvent, the concentration of the complexer is so low that it would be very difficult to detect or identify. Study of the materials that retain plutonium would be difficult and is probably unnecessary since they are formed in such small quantities under conditions normally used in the Purex process. Their formation can be minimized by preventing accumulation of NO_2 in the solvent, as by gas sparging.

4. SUMMARY

Among the compounds formed when NPH is degraded are long-chain nitro, nitrite, and nitroso hydrocarbons. These compounds are detected via ultraviolet, visible, and infrared spectra of the degraded solvents.

A large variety of additional NPH degradation products can be detected by GC-MS. These products include alcohols, unsaturated alcohols, nitro alcohols, nitro alkenes, and esters.

The long-chain aliphatic acids are among the most chemically stable of the degradation products formed. These are detected by potentiometric titration and infrared spectral techniques.

The rate of NPH (initially as ~100% NPH or as 30% TBP~70% NPH) degradation in HNO₃ systems is increased by an increased temperature, the presence of NO₂, and/or an increased HNO₃ concentration. The degradation rate is decreased by the use of an argon sparge to remove NO₂ from the system during the degradation process or by the addition of butanol, which probably acts as an NO₂ scavenger.

The long-chain aliphatic acids produced from NPH degradation appear to present a potentially serious problem. The presence of these compounds at concentrations as low as 1×10^{-3} M can result in serious phase separation problems when degraded solvents are contacted with aqueous Na₂CO₃ wash solutions. The concentration of long-chain acids expected in process solvents may approach this level if no effort is made to remove them.

Chemical degradation of the NPH solvent component with or without TBP present results in small amounts of plutonium retention in Na₂CO₃-washed solvents. Minimizing the total solvent degradation minimizes the plutonium retention.

Overall, the results of this investigation are consistent with previously published literature which report that NPH reacts with radical-like NO₂ molecules in HNO₃ systems and not directly with HNO₃.

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