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Report

# DEGRADATION OF DILUENTS USED WITH TBP IN SOLVENT EXTRACTION

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# DEGRADATION OF DILUENTS USED WITH TBP IN SOLVENT EXTRACTION

by

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## ABSTRACT

The degradation of odourless kerosene and of a range of alternative diluents, in the presence of 20% TBP, by mixtures of nitric and nitrous acids at 60 - 70°C has been investigated. It has been established that the relative extent of degradation can be conveniently and reproducibly measured by a retention test using hafnium with Hf181 as tracer. Alternatives to kerosene and fractions isolated from kerosene, show greater resistance than kerosene itself to nitric acid. The purification of degraded solvent has been studied.

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4. Arrangement of the continuous purification of degraded 20% TBP/OK by alkaline permanganate.

## 1. Introduction

Tributyl phosphate (TBP), which is commonly used after dilution with odourless kerosene (OK) in solvent extraction processes for the treatment of irradiated uranium, produces traces (10 - 100 ppm) of mono- and dibutyl phosphoric acids by radiolysis in the presence of fission product beta and gamma radiation and by thermal de-alkylation in the presence of aqueous nitric acid. These reactions have been studied in detail[1]. and it has been found necessary to purify the solvent before re-use, by agitating with aqueous alkali in order to avoid an accumulation of butyl phosphoric acids. These would reduce the decontamination of uranium and of plutonium from fission products and would cause uneconomic losses of plutonium in raffinates. Experience of large scale chemical processing plants has revealed that the useful life of the solvent can be further limited by unidentified compounds formed by the interaction of nitric and nitrous acids with the diluent under the influence of radiation or at elevated temperatures. Unlike the butyl phosphoric acids, these degradation products are not removed by aqueous alkalis and can slowly accumulate in the solvent. The loss of solvent quality may be reflected in poor phase separation, in decreased mass transfer coefficients for uranium, in the retention of fission products in the solvent after alkali washing and in the persistence of traces of fission products in the uranium and plutonium products. Operational difficulties of this nature have led to the periodic discarding of spent solvent[2]., and to the choice of a less reactive diluent than kerosene in other plants[3,4,5].

Factors which may accentuate diluent degradation in future separation plants are:-

(a) the processing of fuels irradiated to high dosages:

(b) relatively long residence times of solvent and of aqueous phases in the extraction section of the first extractor, imposed by the use of mixer-settler units for the counter-current extraction:

(c) the employment of heated stages.

The work reported here was undertaken to examine the relative stability of odourless kerosene and of several possible alternative diluents towards chemical degradation, to establish a reliable analytical method for determining the extent of degradation and to investigate the possibilities of removing degradation products from used solvent.

## 2. Methods

### 2.1 Solvents

Kerosene and other diluents were used as received from the following sources:-

| | |
|---|---|
| Odourless kerosene, | Shell - B.P. Ltd. (drawn from a 40 gallon stock held by Chemical Engineering Division, A.E.R.E.) |
| n - Dodecane, Source A | Marchon Products Ltd., Whitehaven, Cumberland. |

| | |
|---|---|
| n - Dodecane, Source B | L. Light & Co. Ltd., Colnbrook, Bucks. |
| Shellsol-T (a higher boiling fraction from the synthesis of iso-octane) | Shell Chemical Company, Ltd. |
| Hydrogenated propylene tetramer | Société Progil, Paris. |
| Mepasin (a hydrogenated higher boiling fraction from the Fischer-Tropsch synthesis). | Farbenfabriken Bayer, A.G., Leverkusen, Germany. |

Tributyl phosphate (Albright and Wilson) was washed with aqueous alkali, steam stripped and finally dried in a current of air under reduced pressure.

### 2.2 Solvent degradation

The diluents were used to prepare 20% v/v solution of the dried TBP. Portions (5 - 10 ml) of the TBP solutions were agitated with equal volumes of an aqueous phase containing 1-4M $HNO_3$, 0-0.01M $NaNO_2$ and in certain experiments, sufficient uranium to give 54 g U/l in the solvent. The agitation was carried out in stoppered tubes which were subsequently immersed in a thermostat at 50 - 70°C for periods of 2 - 30 days. No effort was made to exclude air or light from the reaction mixture but all the degradations were carried out under identical conditions; a single experiment (Fig. 2) indicated that photochemical reactions were not taking place. In certain cases the solvent phase was sampled at intervals and the nitrous acid was determined by cerate oxidimetry.

At the end of the desired period of reaction, the contents of the tubes were cooled, transferred to a separating funnel and the solvent layer (which had usually become yellow or brown) was washed twice for 2 minutes with an equal volume of 1M sodium carbonate to remove nitric, nitrous and phosphoric acids and acid esters. The colour of the solvent was intensified by the alkali and a pale colour appeared in the aqueous phase. Emulsification was often observed during the alkali wash and the emulsion was sometimes only broken by prolonged centrifuging. The solvent was finally washed with water. Aliquots were later removed for measurement of Z or H number (see Appendix): there was no evidence of any change in this parameter following long periods of storage of degraded solvent (Table I).

In certain experiments samples of solvents which had undergone the Z or H or Pu retention test and in which the degradation products were therefore saturated with Zr95, Hf181 or Pu239, were used for washing tests with alkali and other reagents.

## 3. Results

### 3.1 Batch experiments with kerosene

Figure 1 shows the course of a typical degradation of odourless kerosene by 4M $HNO_3$ at 70°C. Two different batches of odourless kerosene are seen to vary in their quantitative response, by a factor of about 2. Qualitatively, the reaction shows a period of induction (about 40 hours) followed by a linear increase in degradation with time, up to at least 140 hours. The period of induction could be due to an autocatalytic mechanism involving nitrous acid such as that reported for the nitration of aliphatic hydrocarbons.[6]

Experiments with added sodium nitrite gave no induction period (Fig. 2), while experiments in the presence of a nitrite inhibitor (sulphamic acid) showed no solvent degradation even after 70 hours with 4M $HNO_3$ at 70°C (Table II). Analyses made during the experiments with sodium nitrite showed (Fig. 3) an initial loss of nitrite, followed by a sharp increase to give a concentration higher than that of the sodium nitrite which was added.

The presence of uranyl nitrate in the solvent enhanced the rate of degradation, after a long (150 hours) induction period (Fig. 2). The enhancement may be due to an increased concentration of nitrate ions in the solvent phase in the presence of 54 g uranium l. The autocatalytic production of nitrous acid would eventually produce enough in the aqueous phase to counterbalance the lower partition coefficient into the solvent.

### 3.2 Batch experiments with alternative diluents

The behaviour of certain alternative diluents, whose physical properties are listed in Table II, was studied with 4M $HNO_3$ at 70°C for 70 hours (no nitrite or uranium added). The results (Table IV) show that a saturated hydrocarbon, n-dodecane, is nearly 100 times as stable as the kerosene. n-dodecane does not appear to be commercially available in large quantities: the other diluents, which are more readily available, showed an improvement of between 5 and 23 over kerosene.

It is possible to improve the kerosene by treatments designed to remove minor impurities. Table V gives the results of pre-treatment of kerosene by filtration through alumina, silica gel and other adsorbents. Table VI gives the results of various chemical treatments designed to isolate certain broad classes of hydrocarbons from the kerosene. In general, pretreatment barely narrows the gap between kerosene and the commercially available alternatives and a detailed economic assessment would be required to indicate the cheapest solvent with an acceptable performance. It is assumed that the order of stability of the various diluents towards radiation and chemical attack can be taken from these purely chemical experiments.

### 3.3 Solvent washing

Rather than replace the present odourless kerosene by an alternative and probably more expensive diluent, the normal alkali washing of the recycled solvent could be supplemented by some specific chemical treatment which would prevent the accumulation of kerosene degradation products.

As a control, various alkaline treatments were tested (Table VII) and shown to have practically no effect upon the organic complexing agents responsible for the retention of zirconium and other metals in the solvent. The alkaline washes will however remove most of the retained metals (Table VIII) with the replacement of a heavy metal by sodium to form sodium salts of the organic complexing agents which remain in solution in the organic solvent phase; (see Section 3.4 for confirmation of this hypothesis with Na-24 as a tracer).

The use of solid adsorbents or of ion-exchange resins (Table IX) did not bring about an extensive removal of the complexing agents and in certain cases showed positive disadvantages in the slowness of filtration through the columns and in the loss of TBP by adsorption or by hydrolysis.

Since it seemed possible that the nitroso or keto group was one of the functional groups responsible for the complexing of heavy metals by degraded solvent, a number of condensation reagents such as semicarbazide in aqueous solution were tested as a means of scrubbing the solvent, but with discouraging results (Table X).

Greater success attended the use of strong oxidising agents such as hypochlorous acid or alkaline permanganate (Table XI). The effectiveness of alkaline permanganate supports U.S. work, and was further demonstrated in a counter-current washing experiment (Fig. 4) using 0.05M $Na_2CO_3$, 0.1M $KMnO_4$ at 60°C in a Jackson(7) contactor with a mean solvent residence time of 30 mins. Manganese dioxide, which was precipitated during the washing of the solvent, was partly removed as a suspension in the aqueous raffinate. The smaller fraction of suspended $MnO_2$ which left the contactor with the solvent was removed by a second wash with 0.06M $HNO_3$, also at 60°C. The organic solvent was prepared by diluting a sample of degraded 20% TBP/kerosene, which had been saturated with zirconium-95 and well washed with 0.1M $HNO_3$ to remove TBP-complexed zirconium; with 20% TBP/kerosene in which nitrato complexes of nitrosylruthenium (labelled with Ru-106) had been allowed to age overnight, followed by stripping of less extractable species with 0.1M $HNO_3$. Following the treatment with alkaline permanganate at 60°, the solvent was analysed for Zr95, Ru106 and for Z number and removal factors of 900, 50 and >70 respectively were obtained. Most of the Zr95 and Ru106 which was removed in this process was found to be adsorbed on the $MnO_2$. A potential weakness of any method of solvent washing which relies on oxidation lies in the possibility of oxidising the nitrosylruthenium species to mononuclear ruthenium-IV, which may form a very stable complex with certain products of solvent degradation(8). This mechanism may account for the lower removal of ruthenium than of zirconium in the experiment.

An alternative approach to the problem of solvent washing, the use of organic bases such as ethanolamine, has given encouraging results and is being reported separately(9).

## 3.4 Chemistry of diluent degradation

3.4.1 Shell and B.P. odourless kerosene contains mainly $C_{12}$ straight and branched chain aliphatic hydrocarbons and cyclic hydrocarbons (napthenes) with less than 1% of unsaturated hydrocarbons and between 1 and 2% of aromatic hydrocarbons. In the presence of 20% TBP, the kerosene is slowly attacked by 4M nitric acid at 70°C, whereas straight chain dodecane and a branched chain $C_{11}$ - $C_{13}$ mixture (Shellsol-T) are relatively resistant. The reaction involves autocatalysis by nitrous acid.

3.4.2 TBP is not essential to the reaction - kerosene reacts with oxides of nitrogen at 140° to give similar products but it plays a part as a solvent for nitric and nitrous acids.

3.4.3 The bulk of the reaction products are probably nitro-compounds and or carboxylic acids. A sample of 20% TBP/kerosene after 140 hours in contact with 4M $HNO_3$ at 70°C followed by thorough washing with alkali and water, was yellow-brown in colour and contained 1.3 ± 0.3 w/w nitrogen. This figure would correspond to about 20% conversion of the kerosene to mono-nitro $C_{12}$ compounds. The amounts of strongly reactive complexing agents present are however very small; the solvent gave a Z number of 23,000 i.e. it retained $2.3 \times 10^{-5}$M zirconium equivalent to $9.2 \times 10^{-5}$M of a mono-dentate ligand. Evidence for the presence of particular strong complexing agents rather than a general solvent extraction of heavy metals by nitrated solvent is provided by the constant molar retention index. In the case cited above this was 23,000 for zirconium, plutonium and hafnium respectively under conditions similar to the Z test and 4 x 27,000 for sodium (as Na 24) from 1M $Na_2 CO_3$.

3.4.4 A way to discover the nature of the reactive component in the kerosene and of the reaction product is to separate the heavy metal complexes, say with zirconium or hafnium as gamma-active tracers, from the TBP, kerosene and the nitrated kerosene. The TBP itself is a potent solvent for the metal complexes and is difficult to remove completely by distillation. A useful method for concentrating the degradation products from the reaction of kerosene (in the absence of TBP) with oxides of nitrogen for 1 hour at 140°C, is by washing with 1M sodium carbonate and filtering off the oily solid slowly formed in the kerosene phase. This is soluble in ketones and in TBP, but sparingly soluble in aqueous alkalis. A few hundred milligrammes of this solid was prepared from 200 ml kerosene: it contained complexing agents equivalent to a Z number of 8000 (when made up to 200 ml with 20% TBP). This would correspond to about 0.5 mg of a monodentate ligand if of M.W. 250.

3.4.5 Infra-red analysis of the oily solid (Table XII) showed absorption peaks which are consistent with the presence of a hydroxyl group as water or as undissociated carboxylic acid, of the carbonyl group, of aliphatic - $CH_2$ - , and of the nitro group, there were no signs of the carboxylate group, and the washed oily solid contained no sodium (flame test), indicating that the salt-forming groups were not strongly acidic. The main products of the attack of nitric and nitrous acids or of oxides of nitrogen upon kerosene might be expected(6) to include carboxylic acids, hydroxy and ketonic compounds, nitro and nitroso groups. Some of these main products may interfere with solvent extraction processes - e.g. by acting as emulsifying agents. The retention of fission products such as zirconium must be due to a minor product, probably containing two or more of the functional groups mentioned above, in a favoured configuration and associated with a long hydrocarbon chain. Structural analogies may be taken from familiar analytical reagents such as α-nitroso-β-naphthol, (grouping HO - C - C - N = O), N-nitrosophenylhydroxylamine (grouping HO - N - N = O) and isonitrosoacetophenone (grouping HO - N = C - C = O).

It is unlikely that this minor constituent can be characterised by infrared or vapour phase chromatographic techniques in the presence of large ammounts of other reaction products which contain similar groups. An attempt to isolate the plutonium form of the complex from the bulk of nitro compounds by solvent extraction (in a solvent of low boiling point) from aqueous citrate buffer at pH 9 did not succeed. The plutonium complex was extracted from pH 9 buffer by 20% TBP kerosene but not by benzene or by amyl acetate. TBP also extracted some (but not the major part) of the coloured nitro compounds formed by degradation.

## 4. Conclusions

4.1 The relative degree of chemical degradation of kerosene and similar materials by nitric and nitrous acids under various conditions can be estimated reliably by measuring the retention of quadrivalent heavy elements in a standardised test. Details are given of a test which is reproducible, gives low 'blanks' on untreated solvent and yields a constant molar index whether zirconium, plutonium or hafnium is used as the tracer.

4.2 The presence of TBP is not essential to the degradation reaction, since kerosene itself gives similar products, with oxides of nitrogen at 140°C.

4.3 The degradation of odourless kerosene mixed with 20% of TBP, by 4M $HNO_3$ at 70°C requires an induction period of 40 hours during which nitrous acid is produced. The reaction is suppressed completely in the presence of sulphamic acid or of a similar nitrite inhibitor.

4.4 The rate of degradation, in the presence of nitrous acid, increases with temperature and with the nitrate concentration (nitric acid or uranyl nitrate) in the solvent phase.

4.5 The rates of degradation of n-dodecane, Shellsol-T, hydrogenated propylene tetramer, and mepasin are less than that of odourless kerosene by factors of 100, 25, 8, and 5 respectively.

4.6 Pre-treatment of odourless kerosene by oleum washing, by steam distillation with the rejection of the less volatile fraction, by the urea - occlusion process to isolate the straight chain paraffins or by combinations of these processes improved the quality by factors of from 2 to 8.

4.7 Solvent which has been allowed to degrade may be recovered for re-use by treatment with oxidising agents, particularly with alkaline permanganate at 60°C for 30 mins. The permanganate is reduced to manganese dioxide, which carries any zirconium and ruthenium fission products which were present in the solvent.

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## TABLE I

Measurements of the retention of heavy metals by degraded 20% TBP/OK solvent

| Batch of degraded solvent | Date of analysis | $\times 10^{-9}$ molar | | |
|---|---|---|---|---|
| | | Zr retention | Hf retention | Pu retention |
| A | 5.6.59 | | | 23,500 |
| " | 8.8.59 | 26,600 | | |
| " | 28.10.59 | | 21,900 | |
| " | 23.2.60 | 23,000 | | |
| " | 10.2.60 | | 23,100 | |
| " | 27.5.60 | | 22,100 | |
| B | 10.2.60 | | 1,400 | |
| " | 21.7.60 | | 1,360 | |
| " | 9.9.60 | | 1,320 | |
| " | 20.10.60 | | 1,330 | |

## TABLE II

## Suppression of degradation reaction by a nitrite inhibitor

($4M\ HNO_3$, 70°C in contact with 20% TBP/OK for 70 hours.

(Untreated solvent gave Z=18).

| Sample of kerosene | Additives to aqueous $HNO_3$ | Z number of solvent product* |
|---|---|---|
| Batch A | Nil | 5500 |
| | 1M $NaNO_2$ | 5700 |
| | 1M Sulphamic Acid | ~ 15 |
| Batch B | Nil | 9500 |
| | 1M $NaNO_2$ | 9050 |
| | 1M Sulphamic Acid | ~ 30 |

*The Z number of a solvent is the number of moles of zirconium which are retained in $10^9$ litres of the solvent.

# TABLE III

## Physical properties of diluents

| Diluent | Density | Boiling range °C | Flashpoint by Pensky-Martens Closed Cup at Esso Research Ltd., Abingdon |
|---|---|---|---|
| Odourless kerosene (Shell B.P.) | 0.784 | 195 - 262°C | 77.5°C |
| n-dodecane | 0.766 | 214 | 73 |
| Shellsol-T | 0.763 | 185 - 210 | 60.5, 62 |
| Hydrogenated propylene tetramer | 0.762 | 160 - 220 | 67.5 |

# TABLE IV

## Extent of degradation of different diluents

($4M\ HNO_3$, 70°C, 70 hrs)

| Diluent | Z or H Number |
|---|---|
| Odourless kerosene, Batch A (Windscale) | 5500 |
| Odourless kerosene, Batch B (AERE Chem. Eng. Division) | 9500 |
| Commercial n-dodecane | 394 |
| Laboratory purified n-dodecane | 100 |
| Shellsol-T (a higher boiling fraction from synthesis of iso-octane) | 409 |
| Mepasin (a hydrogenated Fischer-Tropsch fraction) | 2070 |
| Hydrogenated propylene tetramer | 1220 |

# TABLE V

## Performance tests on pre-treated kerosene

(Made up to 20% TBP and reacted with 4M $HNO_3$ for 80 hours at 70°C)

| Treatment | Z number | Improvement factor* |
|---|---|---|
| Control (untreated) | 7630 | 1 |
| Activated alumina (first few throughputs) | 1590 | ~5 |
| Activated alumina (after 30 throughputs) | 4520 | 1.7 |
| Activated charcoal | 8040 | 1 |
| Silica gel | 3970 | ~2 |
| Linde molecular sieve 4A | 5670 | 1.4 |
| Chromatography grade cellulose | 10,500 | 1 |
| Powdered urea crystals | 6730 | 1.1 |
| Dried and powdered clay soil | 3640 | ~2 |

*Improvement factor = $\frac{\text{Z number before treatment}}{\text{Z number after treatment}}$

## TABLE V (continued)

### Performance tests on pre-treated kerosene

| Treatment of kerosene | Improvement factor |
|---|---|
| Alkaline $KMnO_4$, 20°, 10 mins. | 2.5 |
| Acid " " " | 1.0 |
| Chromic acid solution, 20°, 4 hrs. | 2.5 |
| 20% Oleum, 20°, 2 hours | 2.4 |
| " " " 4 hours | 2.4 |
| Straight chain paraffins isolated by urea occlusion | 3.4 |
| As above, followed by 20% oleum, 20°, 2 hrs. | 7.9 |
| Branched chain paraffins, residue from urea occlusion | 0.5 |
| First fraction from steam distillation of kerosene | 3.0 |
| Residue after steam distillation of most of the kerosene | 0.2 |

## TABLE VI

## Effect of alkali washing upon organic complexing agents in degraded 20% TBP/OK solvent

| Reagent | Temperature $^{\circ}C$ | Duration of treatment | Improvement factor |
|---|---|---|---|
| 1M $Na_2CO_3$ | $45^{\circ}$ | 30 mins | 1 |
| 1M NaOH | $45^{\circ}$ | 10 mins each 4 successive washes | 1 |
| 1M $Na_2CO_3$ | $20^{\circ}$ | 14 days | 1.7 |

## TABLE VII

## Removal of retained metals from degraded 20% TBP/OK solvent by 1M sodium carbonate solution at 20°C

| Metal | Duration of washing with carbonate | Removal factor from solvent |
|---|---|---|
| Zr | 0.5 hrs | 2.5 |
| | 1.5 hrs | 3.4 |
| | 5 hrs | 5.3 |
| Pu | 0.5 hrs | 11 |

## TABLE VIII

## The purification of degraded 20% TBP/OK solvent using solid adsorbents or ion exchange resins

| Treatment (at 20°C) | Volume of Solvent treated (Column volumes) | Improvement factor | Notes |
|---|---|---|---|
| (Control) | | 1 | % TBP = 20 |
| Zeo-Karb 225<br>(cation resin, H form) | 1 | 2 | % TBP = 20 |
| De-Acidite FF | 1 | 1.3 | |
| (anion resin, HO form) | 10 | 1.4 | % TBP.= 17 |
| Bio-deminrolite<br>(mixed-bed resins) | 1 | 4 | Loss of TBP observed |
| Mixture of solid $KMnO_4$ and $NaHCO_3$ | 1 | 12 | Blockage by $MnO_2$ gives very slow flow rate |
| Zirconium phosphate | 1 | 0.9 | |
| | 10 | 1.0 | % TBP = 19 |
| Activated charcoal | 1 | 4 | |

## TABLE IX

## Attempts to destroy the organic complexing compounds in degraded 20% TBP/OK solvent using condensation reagents

| Reagent (1 equal volume wash) | Temperature °C | Duration of treatment | Improvement factor |
|---|---|---|---|
| 50% w/w hydrazine in 1M $Na_2CO_3$ | 20°C | 1 hr | 1.1 |
| Semi carbazide hydrochloride in 1M $Na_2CO_3$, pH 8.4 | " | 1 | 1.0 |
| Satd. sulphamic acid in pH 9.3 buffer | " | 1.25 | 1.0 |
| Satd. sulphamic acid | " | 2 | 1.4 |
| " " | 0° | 1 | 1.4 |
| " " | 100° | 2 | 1.2 |
| Satd. acetamide (pH 5.5) | 20° | 1 | 1.5 |

## TABLE X

## Attempts to destroy the organic complexing compounds in degraded 20% TBP/OK solvent using oxidising or reducing reagents

| Reagent (1 equal volume wash) | Temperature °C | Duration of treatment hrs. | Improvement factor |
|---|---|---|---|
| 10% $K_2Cr_2O_7$ in 50% $H_2SO_4$ | 21 | 0.5 hrs | 4 |
| 100 vol. $H_2O_2$ | 100 | 2 hrs | 2 |
| 1M NaOCl, satd. with $Cl_2$, pH 4.1 | 20 | 0.1 | 10 |
| | | 0.5 | 25 |
| | | 1 | 25 |
| | | 1.5 | 25 |
| | | 3 | 9 |
| 1M NaOCl, satd. with $Cl_2$, pH 9 | " | 0.5 | 4 |
| 1M NaOCl, pH 11 | " | 0.5 | 3 |
| 1M chloramine-T pH 8.5 | " | 1 | 2 |
| 0.05 N $KMnO_4$ + 0.5M $Na_2CO_3$ | " | 0.25 | 5 |
| Granulated zinc, 6M HCl | " | 1.5 | 3 |
| 50% w/w hydrazine nitrate | " | 1.5 | 3 |
| " | 90 | 2 | 1 |
| 1M ferrous sulphamate | 20 | 0.5 | 1.7 |

# TABLE XI

## Infrared absorption bands in degraded kerosene

| Carbonate Washed Material | | Carbonate Extract | |
|---|---|---|---|
| Frequency ($cm^{-1}$) | Assignment | Frequency ($cm^{-1}$) | Assignment |
| 3300 - 2700 m,b | -O-H str. (of $-C{<}^{O}_{OH}$) | 3200 s,b | or $H_2O$<br>-O-H str. (of $C{<}^{O}_{OH}$) |
| 1708 m. | C=O str. (of $-C{<}^{O}_{OH}$) | 2920 and 2837 s.<br>1708 s. | C-H str.<br>C=O str. (of $C{<}^{O}_{OH}$) |
| 1626 w. | (-O) $NO_2$ as. str. (nitrate) | | |
| 1548 s,sp | $NO_2$ as. str. (nitro) | 1543 m. | $NO_2$ as. str. (nitro) |
| 1461-1433 m | C-O str. or OH def. ? | 1455 s. ) | C-H def. |
| | | 1373 s. ) | |
| 1385 w. ) | C - H def.<br>(of nitro deriv.) | | |
| 1365 sh. ) | | (Diffuse absorption beyond 1373) | |
| 1351 m. | $NO_2$ sym. str. (nitro) | | |
| 1272 vw. | (O) $NO_2$ sym. str. (nitrate) | | |
| 853 m,b | C - N def. | | |

s = strong, m = medium, b = broad, w = weak, sp = sharp, v = very, sh = shoulder,

as = asymmetric, str = strength, def = deformation, sym = symmetric.

# APPENDIX

## The Z or H index of solvent quality

The procedure in use at A.E.R.E. is as follows:-

1. An aliquot of the solvent is vigorously stirred for two minutes with an equal volume of 1M. $Na_2CO_3$ solution, the mixed phases are then centrifuged for one minute and the aqueous phase discarded.

2. Repeat of stage 1.

3. The solvent phase is then equilibrated with an equal volume of $3M.HNO_3$ for two minutes and the aqueous phase discarded.

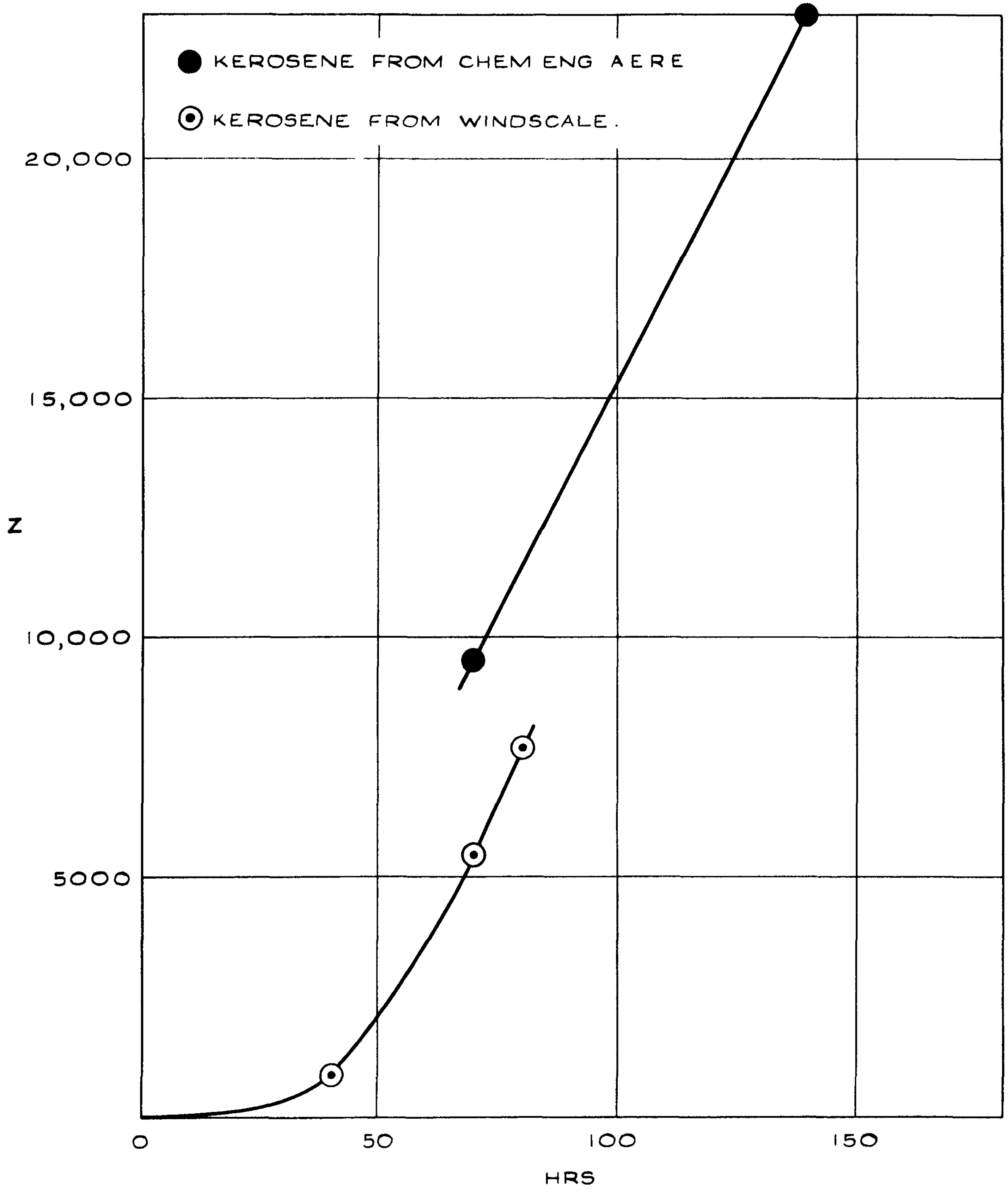
4. The solvent phase is stirred for five minutes with an equal volume of $3M.HNO_3$ containing $10^{-3}$M. $Zr/Zr^{95}$ or $Hf^{181}$, the phases are separated and the aqueous phase discarded.

5. The solvent containing $Zr^{95}$ or $Hf^{181}$ is then stripped with six, equal volume, five minute scrubs with $3M.HNO_3$.

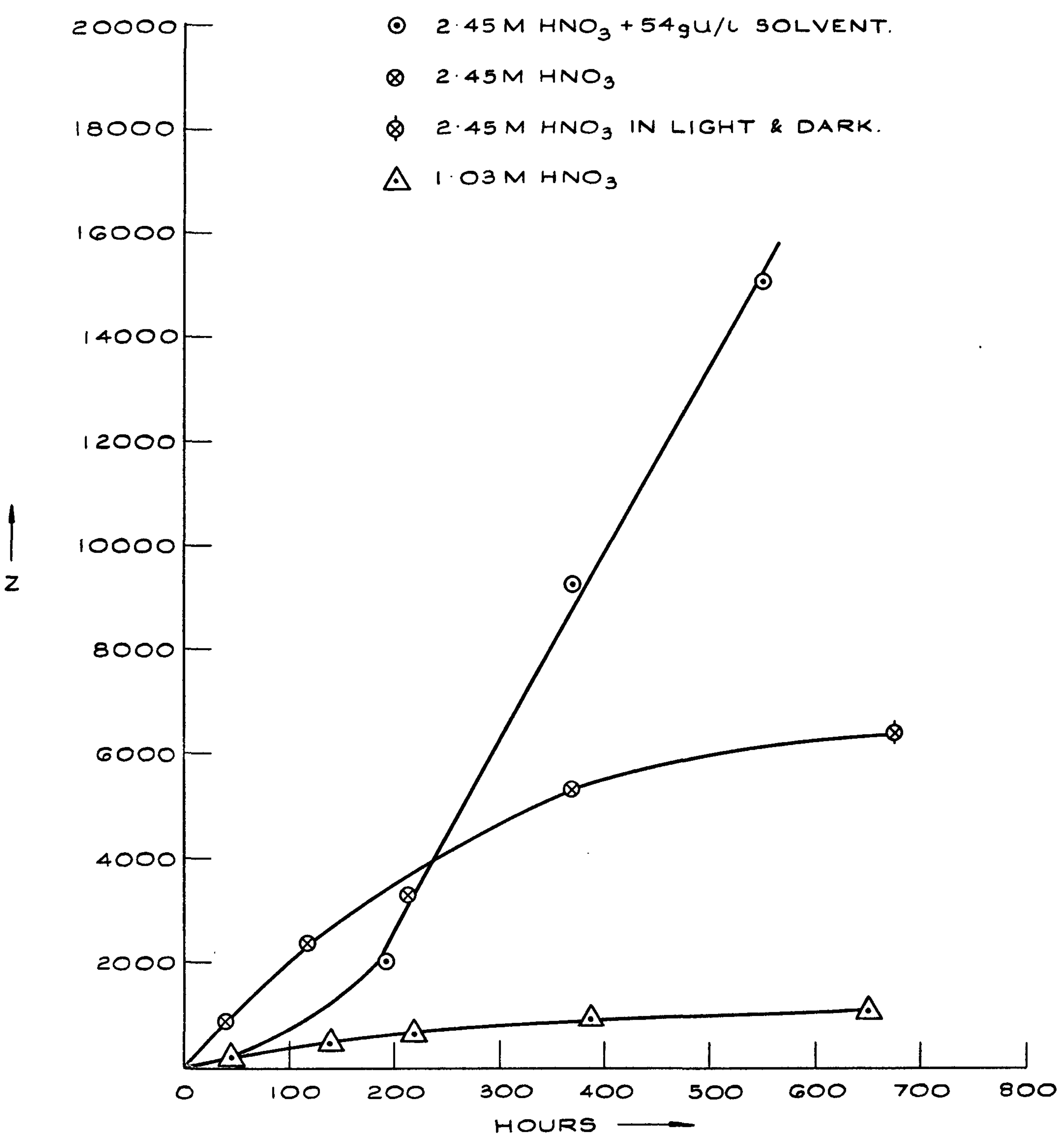
6. The solvent is centrifuged for one minute and an aliquot mounted for $\gamma$ counting.

## Calculation of the Index

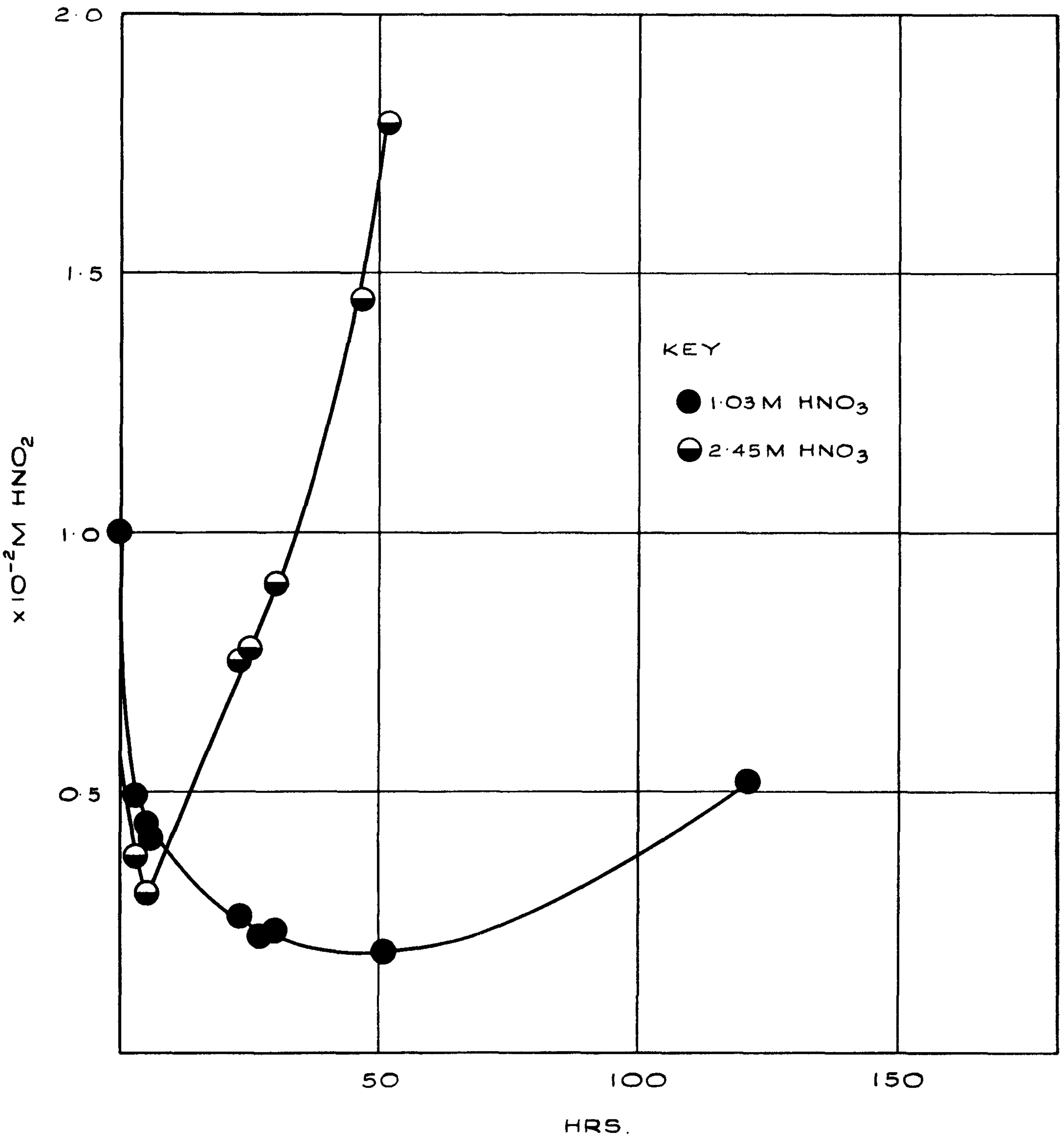
The specific activity of the $3M.HNO_3$ solution containing $10^{-3}$M. $Zr/Zr^{95}$ or $Hf^{181}$ is determined by $\gamma$ counting an aliquot of a hundred time diluted solution; from this result the correlation between $\gamma$ counts and moles of Zr of Hf is obtained. Hence from the result of stage 6, the number of moles retained by the aliquot taken can be calculated; this is related to the number of moles of Zr or Hf that would be retained by $10^{9}$ litres of solvent and this figure is called the H number if Hf was used, or the Z number if Zr was used, in the retention test.



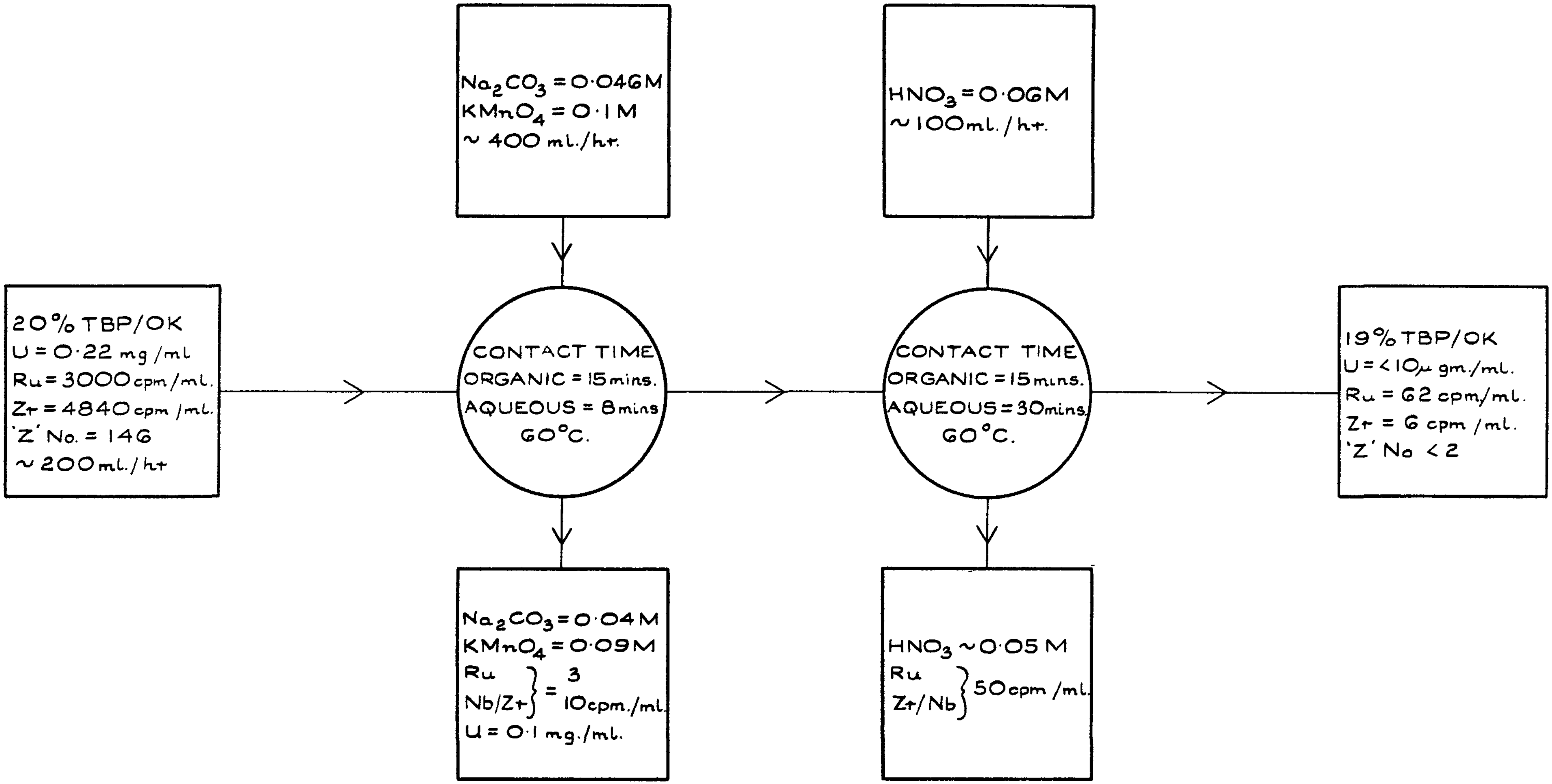
A.E.R.E. R. 3507. FIG. I. DEGRADATION OF 20% TBP/OK SOLVENT BY 4 M $HNO_3$ AT 70°C. NO ADDED NITRITE.



A.E.R.E. R.3507. FIG. 2. DEGRADATION OF 20% TBP/OK BY 1·03M AND BY 2·45M $HNO_3$ AT 60°C. INITIAL ADDITION OF $10^{-2}M\ HNO_2$.



A.E.R.E. R. 3507. FIG. 3. NITROUS ACID CONTENT OF 20% TBP/OK IN CONTACT WITH 1·03M AND 2·45M HNO$_3$ AT 60°C. (1 x 10$^{-2}$M NITROUS ACID ADDED INITIALLY.)



A.E.R.E. R. 3507. FIG. 4. ARRANGEMENT OF THE CONTINUOUS PURIFICATION OF DEGRADED 20% TBP/OK BY ALKALINE PERMANGANATE.