matogram peaks, and the infrared spectra were obtained in carbon disulfide after evaporating the cyclohexane with a stream of nitrogen from a syringe needle. The preferred sample size for injection into the column appeared to be from 5 to 50 mg. Samples were injected through a *T* fitting in the line just preceding the packing.

RESULTS

A large number of runs was made on this column without changing the packing, without using any carrier fluid other than spectral grade cyclohexane and without subjecting the packing to any treatment. A wide variety of aromatic hydrocarbon samples, synthetic mixtures, and neutral oil fractions were examined with this column. Retention volumes for the same components were found to be identical within the ability to read the charts. Under the conditions described, the volumes could be read without difficulty to the nearest 50 drops. There was 11.5 ml. of cyclohexane in each 400-drop fraction.

Figure 1 shows the results for a 12.1-mg. sample of 1,2-dimethylnaphthalene described as "pure." The first peak was produced by an impurity (ultraviolet and infrared spectra indicated 3-methyl biphenyl), and the second peak was produced by 1,2-dimethylnaphthalene. Figure 2 shows the results for a synthetic mixture of 9.4 mg. of acenaphthene and 9.9 mg. of acenaphthylene, the compounds being eluted in this order. The retention volumes for these three compounds are summarized in Table I. The volumes for the same compound on different runs were found to be identical even when these runs were separated by runs on other samples.

Table I. Retention Volumes of Some Aromatic Hydrocarbons on Alumina Containing 4.09 Wt. % Water

Compound	Run no.	Retention vol., cyclohexane, drops
Acenaphthene	16	7800
	17	7800
1,2-Dimethylnaphthalene	6	8000
	10	8000
Acenaphthylene	11	9750
	16	9750
	17	9750

These results, and others to be reported in more detail at a later date, indicate that if liquid chromatography is used under operating conditions fully analogous to those for gas chromatography, much the same can be accomplished in analysis. In addition, liquid chromatography can be used with nonvolatile or thermally sensitive compounds.

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Reaction of Triethylamine at Platinum Anodes in Acetonitrile Solution; Solvent Background with Perchlorate Supporting Electrolyte

SIR: Some preliminary results in a study of the reaction of aliphatic amines at platinum anodes in acetonitrile may be of general interest. This reaction has been used to advantage by Streuli (*6, 10*) in the development of a coulometric titration procedure for organic bases. While Streuli considered the net anodic reaction to be the oxidation of water (present in solution from 0.05*M* $LiClO_4 \cdot 3H_2O$ supporting electrolyte) to yield hydrogen ion, Billon (*1, 2*) describes similar results obtained in anhydrous $LiClO_4$ solution and attributes the titration to hydrogen ion generated quantitatively in the anodic background reaction of acetonitrile.

The anodic background reaction at platinum electrodes in acetonitrile solutions of perchlorate salts is still the subject of controversy in spite of the growing interest in the use of acetonitrile as an electrochemical solvent and the frequent use of perchlorate supporting electrolytes in nonaqueous media. Schmidt and Noack (*9*) proposed the following reaction scheme

$$ClO_4^- \rightarrow ClO_4\cdot + e^- \qquad (1)$$

$$CH_3CN + ClO_4\cdot \rightarrow \cdot CH_2CN + HClO_4 \qquad (2)$$

$$2\cdot CH_2CN \rightarrow NCCH_2CH_2CN \qquad (3)$$

and reported quantitative generation of hydrogen ion at the anode.

Maki and Geske (*8*) and Billon (*2*) have reported an electron spin resonance spectrum of the reaction intermediates which they attribute to perchlorate radical. Billon (*2*) was unable to detect succinonitrile in the electrolysis products and disputes reaction 3 of the Schmidt-Noack sequence, although Schmidt and Noack reported the detection of succinonitrile in the reaction mixture by conversion to pyrrole. No yield of pyrrole was given.

Evidence from this laboratory now indicates that the anodic background reaction involves degradation of perchlorate to lower oxidation states of chlorine, and that the presence of triethylamine completely alters the course of the reaction. The amine appears to participate actively in the electrode reaction instead of serving as the passive proton acceptor envisioned by previous workers. The evidence may be summarized as follows:

(a) Perchlorate destruction at the anode, determined gravimetrically by precipitation of methylene blue perchlorate (*11*), amounted to 0.20 mole/faraday in 0.1*M* $NaClO_4$ and 0.13 mole/faraday in 0.1*M* $NaClO_4$ + 0.2*M* H_2O. Qualitative tests showed that a small amount of chloride ion was formed.

(b) Addition of triethylamine to the solution in the anode compartment of the electrolysis cell completely inhibited the destruction of perchlorate.

(c) Triethylamine produced a well defined irreversible anodic chronopotentiometric wave in an anhydrous acetonitrile solution of tetraethylammonium perchlorate.

(d) Potentiometric titration of the acid produced by the anodic background reaction in 0.1*M* $NaClO_4$ solution indicated the formation of a mixture of $HClO_4$ and weaker acids. Current efficiency for strong acid generation was 90 to 95%; for total acid generation, 105 to 110%. This should be compared with the accuracy of better than 1% attained by Streuli in his coulometric titration of bases.

(e) Chronopotentiometry with current reversal indicated a current efficiency for strong acid formation of only about 70%.

It appears likely that reaction 1 of the Schmidt-Noack sequence does occur, but that it is followed by oxidative chemical attack of the perchlorate radical on the solvent. A mixture of products probably results, in view of the observed fact that a fraction of the perchlorate is reduced all the way to chloride. The g-factor and coupling constant reported by Maki and Geske for perchlorate radical agree with those since reported by Cole (*3*) for chlorine dioxide and the liftetime of the observed radical, measured in seconds, seems longer than one might expect for perchlorate free radical.

Formation of chloride ion explains the effectiveness with which anodization in acetonitrile solutions of perchlorates cleans a platinum electrode, since some dissolution of the platinum can be expected. This phenomenon was reported by Hoh, McEwen, and Kleinberg (*7*) and has been used to advantage by the author in obtaining reproducible electrode surfaces.

Possibly the net anode reaction in the presence of triethylamine is that proposed by Streuli or by Billon, if the mechanism is the following:

$$(C_2H_5)_3N \rightarrow (C_2H_5)_3N\cdot^{+} + e^{-} \qquad (4)$$

$$(C_2H_5)_3N^{+}\cdot + \left\{\begin{matrix} CH_3CN \\ H_2O \end{matrix}\right\} \rightarrow (C_2H_5)_3NH^{+} + \left\{\begin{matrix} \cdot CH_2CN \\ \cdot OH \end{matrix}\right\} \qquad (5)$$

Cyanomethyl radicals, if formed, could couple head-to-head to form succinonitrile or head-to-tail (*5*) to form *N*-cyanomethylketenimine. Hydroxyl radicals could couple to form hydrogen peroxide and be further oxidized to oxygen. The detailed reaction is currently being studied in this laboratory. A full description of the experiments mentioned in this communication will be published later.

Since the submission of this communication, a study of amine oxidation at platinum anodes in dimethylsulfoxide has been published by Dapo and Mann (*4*), reporting a reaction sequence which parallels reactions 4 and 5. This reaction sequence can account for Streuli and Hanselman's successful use of the glass electrode as end point indicator and was suggested by reverse-current chronopotentiometric data obtained in this laboratory.

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Determination of Nitrate in Water by Ultraviolet Spectrophotometry

Sir: The strong absorption of the nitrate ion near 203 mμ (*2*) has been used for determination of nitrate in natural waters (*3, 4*). In these methods, the absorbance of the sample is measured at 210 or 220 mμ where nitrate absorbs strongly, and also at 275 mμ where its absorption is negligible. By subtracting a multiple of the absorbance at 275 mμ, as a correction for organic matter, from that at the shorter wavelength, the absorption due to nitrate is estimated.

This method of correction is justifiable if the nonnitrate absorption at 210 or 220 mμ is small, but this is not so for some natural waters or for sea water, the absorbance of which increases steeply at wavelengths shorter than 235 mμ (*1*).

The addition of an equal volume of concentrated sulfuric acid to a solution containing nitrate, when chloride is also present, causes a change in the nitrate absorption spectrum, the maximum being shifted to around 230 mμ. The determination of nitrate by measurement at this wavelength is easier because the absorption of other substances is a good deal less than at 210 mμ, and may even be diminished in the presence of the sulfuric acid. Moreover the high acid concentration greatly increases the reactivity of nitrate so that it may be destroyed by a suitable reducing agent, and so allow accurate measurement of the nonnitrate absorbance of the solution.

EXPERIMENTAL

Apparatus. A Beckman DK 2 recording spectrophotometer or Unicam SP 500 spectrophotometer was used.

Reagents. Sulfuric acid 98%. Reagent grade acid, sp. gr. 1.84, is heated to boiling for 15 minutes, cooled, and stored in a glass-stoppered bottle.

Hydrazine sulfate. Two grams of $N_2H_4 \cdot H_2SO_4$ are dissolved in water and made to 100 ml.

Standard nitrate. KNO_3, 1.01 grams, is dissolved in water and made to 1 liter. One milliliter is defined as 10 μg. atom or 140 μg. of N.

Recommended Method. The sample should contain not more than 2.5 p.p.m. of nitrate–nitrogen but more than 2 grams of chloride per liter. Samples of higher nitrate concentration may be diluted with 0.1*M* HCl. If the chloride concentration is too low, hydrochloric acid may be added—e.g., with potable water of negligible chloride content it is convenient to add 0.5 ml. of 11*M* HCl to a 100-ml. sample.

In each of two 150- × 20-mm. stoppered test tubes place 10 ml. of sample, and to one portion add 0.1 ml. of hydrazine sulfate solution. From a buret, with the tap lubricated only with sulfuric acid, add to each tube 10 ml. of sulfuric acid, taking care that mixing is not sufficient to cause the solution to boil. Stopper the tubes, cool in running water, mix, and cool again. Measure the absorbances at 230 mμ. The difference in the two readings is proportional to the nitrate concentration. A factor for the calculation may be obtained by carrying samples with a known addition of nitrate through the process.

A blank on the sulfuric acid, using 0.1*M* HCl with and without hydrazine sulfate is necessary to show whether nitrate in the acid is present in significant amount. If so, it will be included in the result for the sample, and a correction must be applied. Traces of organic matter in the sulfuric acid may increase its ultraviolet absorption appreciably, and it is essential to destroy them by boiling the acid before use.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of nitrate and nitrite in water and in 50% v./v. sulfuric acid. Figure 2 shows the spectra in 50% v./v. sulfuric acid when the chloride concentration is 0.05*M*. Nitrate and nitrite give almost identical spectra with a broad maximum