as any free chloride is present in the solution. The reaction $Cr^{+3} + Cl^- \rightarrow CrCl^{+2}$ is sufficiently slow that this source of $CrCl^{+2}$ may be neglected. The possibility that two chloride ions are present in the transition state, although not likely, cannot be absolutely eliminated because of the rapid rate of the reaction (*7*):

$$CrCl_2^+ + Cr^{+2} \rightleftharpoons Cr^{+2} + CrCl^{+2} + Cl^-$$

When the oxidation is carried out in the presence of both chloride and iodide, the iodide [which is more strongly adsorbed on mercury than is chloride (*4*)] can replace chloride in the transition state even when chloride is present in excess of both iodide and chromium. Thus, for example, electrolysis of 50 ml. of a solution containing 1.0 meq. Cl^-, 0.1 meq. I^-, and 0.7 meq. Cr(II) resulted in the production of only 0.5 meq. $CrCl^{+2}$ instead of the 0.7 meq. $CrCl^{+2}$ that would have resulted if no iodide had been present (Figure 1).

DISCUSSION

The results of the controlled potential oxidation of Cr(II) in the presence of chloride require that chloride be bound to chromium in the transition state. Zwickel and Taube (*8*) have shown that chloride enhances the rate of oxidation of Cr^{+2} by $Co(NH_3)_6^{+3}$ and that the product of the reaction by the chloride-dependent path is $CrCl^{+2}$. This indicates that catalysis of the oxidation of Cr^{+2} by chloride with formation of $CrCl^{+2}$ need not imply an inner-sphere, bridged-complex mechanism. But in the case of oxidation of Cr(II) at mercury electrodes in the presence of chloride, a bridged, inner-sphere complex can be formed, and since this is the usual mechanism for oxidation of Cr(II) in homogeneous solution, it is reasonable to assume that it is favored here.

The fact that chloride has little effect on the rate of the homogeneous Cr^{+2}-Cr^{+3} exchange reaction (*3*) suggests that the rate enhancement observed by Aikens and Ross is due to formation of a bridged, activated complex between Cr^{+2} and chloride adsorbed on the mercury electrode, rather than reaction at the electrode of $CrCl^+$ whose equilibrium concentration is extremely small. The analogy between chloride adsorbed on mercury electrodes and the chloride in complex ions—e.g., $Co(NH_3)_5Cl^{+2}$—in which it is known that chloride serves as a bridge for electron transfer, is sufficiently clear to make this a reasonable and attractive hypothesis. In the chloride-iodide competition experiment described, 91% of the halide present is chloride; yet only 71% of the Cr(II) oxidized is $CrCl^{+2}$. According to the above point of view, the distribution of product between CrI^{+2} and $CrCl^{+2}$ should be controlled by the surface concentration ratio of chloride to iodide on the mercury electrode. Since iodide is more strongly adsorbed on mercury than is chloride, this result is at least qualitatively explained by the proposed mechanism.

Chronopotentiometric and oscillopolarographic studies of the oxidation mechanism of Cr(II) are currently in progress to try to settle this and other related questions.

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Large Volume Activation Analysis of Organically Bound Iodine Using Isotopic Neutron Sources

SIR: The analysis of organically bound halogens is especially tedious and time consuming. A method for the determination of organically bound iodine by the technique of neutron activation analysis was developed with specific reference to acetrizoic acid.

In conventional methods of activation analysis using isotopic neutron sources, a small sample is placed at a distance from the source, and the efficiency of utilization of neutrons is very low. Thus, a limiting factor in the precision of such techniques is the total number of counts which can be obtained from the activated species to estimate the desired constituent. In the work reported herein, macro volumes and concentrations were used and an activation analysis technique adapted to the sample. An isotopic neutron source was immersed directly in the sample solution to give 4-pi absorption of neutrons. The sample solution served as a moderator for the neutrons. This also allowed for the absorption of neutrons at the resonance energies of the species to be activated, where neutron absorption cross section increases greatly (*10*). Subsequently the activity of a liter of activated sample was counted using a large volume liquid scintillation counter. Preliminary calibration curves of induced activity were prepared. This method of irradiation and counting increased the number of counts per unit time per unit concentration over conventional methods, thus improving sensitivity and precision. The complete analysis can be carried out in less than 1 hour.

Iodine-127 is the only naturally occurring isotope of iodine. It has a thermal neutron activation cross section of 5.6 barns (*12*) and reacts to form I^{128} by the (n,γ) reaction (*5*). Iodine-128 has a half life of 25 minutes and decays through beta, gamma, and electron capture processes.

The determination of iodine by neutron activation analysis has been investigated by several workers (*2, 3, 5, 6, 15, 16*). In particular, Tsuji *et al.* determined organically bound iodine by placing a 5-ml. sample externally to a 50-mc. Ra-Be neutron source. In this case, the small sample size and relatively low source activity resulted in activation levels which were too low to give good precision.

Another method of analysis has been suggested by Kabasakalian and McGlotten (*11*), who made a study on the polarographic behavior of ten iodinated x-ray contrast compounds.

EXPERIMENTAL

Apparatus and Reagents. An x-ray contrast compound, acetrizoic acid (Urokon Sodium) (3-acetylamine-2,4,6,-tri-iodo benzoic acid), was used as the source of organically bound iodine. This compound contains 68.35% iodine by weight. The official method of analysis for iodine

in acetrizoic acid, as listed in the USP XVI (*13*), involves the digestion of the sample for 18 hours to free the iodine. Since acetrizoic acid is a fairly insoluble powder, the sodium salt was used to carry out the activation study.

The activation containers were fabricated from metal cans 4 inches in diameter by 8 inches long. The 4-pi absorption of neutrons was made possible by mounting a Bakelite tube, 8 inches long and 1.125-inches i.d., through the center of the container. Pouring spouts were mounted at one end. This provided a solution thickness of 1.375 inches around the source tube and a total volume of 1340 ml.

Four 1-curie Pu-Be neutron sources were used to accomplish activation. The dimensions of each source were 1.062 inches in diameter by 1.6 inches long. The four sources thus occupied a tubular space of 1.062 inches in diameter by 6.4 inches long. The total neutron yield from the sources was 7.23×10^6 neutrons per second (*9*). A tubular source holder for positioning the sources was constructed from a sheet of polyethylene, allowing the sources to be centered in the activation container.

De and Meinke (*3*) stressed the importance of paraffin surrounding an isotopic neutron source for the optimum utilization of neutrons. Preliminary studies with our system showed that a 56% increase in the activity of the irradiated solutions was caused by use of a paraffin reflector (*7*). A cylindrical paraffin block 16 inches in diameter by 10 inches high with a 4-inch diameter hole through the center served as the main neutron reflector. With additional 6-inch thick blocks on the top and bottom of this cylindrical block, the activation container was completely surrounded by paraffin. The complete irradiation setup is shown in Figure 1.

The activated samples were counted in an external-sample, 4-pi, large volume liquid scintillation counter (*4*). The sample chamber was 4 inches in diameter by 8 inches long and could readily accommodate a liter of sample.

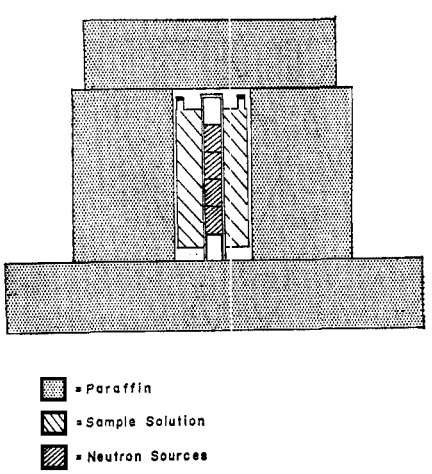

Figure 1. Cross-sectional view of irradiation setup showing source and sample container surrounded by paraffin reflector

Procedure. Sodium acetrizoate solutions were prepared in concentrations of 10, 12.5, 15, 30, and 50% (weight to volume) following a procedure described by the Mallinckrodt Chemical Co. (*8*). A paste of acetrizoic acid is made with distilled water and is slowly neutralized with a 20% NaOH solution. The final pH is adjusted to 7.5 with dilute acetic acid. The solution is then brought to volume.

To evaluate the relationship between concentration and induced activity over a 50% concentration range, all 5 solutions of the sodium acetrizoate were analyzed. Each 1340-ml. sample was irradiated for 20 minutes. One liter aliquants of the activated samples were transferred to polyethylene containers and each was counted for 1 minute, beginning 9 minutes after irradiation.

In all cases, the procedure was repeated three times with the same samples, with sufficient time allowed for complete decay of previously induced activity.

RESULTS AND DISCUSSION

Over a concentration range from 10 to 50% sodium acetrizoate, a curvilinear relationship between concentration and activity was found as shown in Figure 2. As the concentration increased, the specific activity (c.p.m. per unit concentration) decreased. The decrease in specific activity was attributed to the self-shielding effects resulting from the high concentration of iodine in each sample (*14*).

Figure 2 shows that, over more limited concentration ranges, such as from 10 to 15%, the relationship between concentration and induced activity may be taken to be linear.

Sodium acetrizoate contains 3.97% sodium by weight. Although the cross section of Na^{23} is relatively small (0.55 barns) (*12*) and the half life of the resulting Na^{24} relatively long (15 hours), some sodium activation is to be expected. In separate experiments using NaI, it was determined that each gram of Na^{23} results in 350 c.p.m. for the same irradiation and counting times described above. However, since the ratio of sodium to iodine in the molecule remains constant at all times for a given compound, the technique will be valid so long as the calibration curves are prepared using the same substance as that to be analyzed.

The limiting errors in the precision of the technique are the statistical counting errors. The standard deviation was calculated on the basis of a 1-minute sample count and two 1-minute background counts for each sample.

If the net counting rate, N_1, due to the source is $N_1 = N_2 - B$, where B is the background counting rate and N_2 is the gross (sample + background) counting rate, then the standard deviation in N_1 is just (*1*):

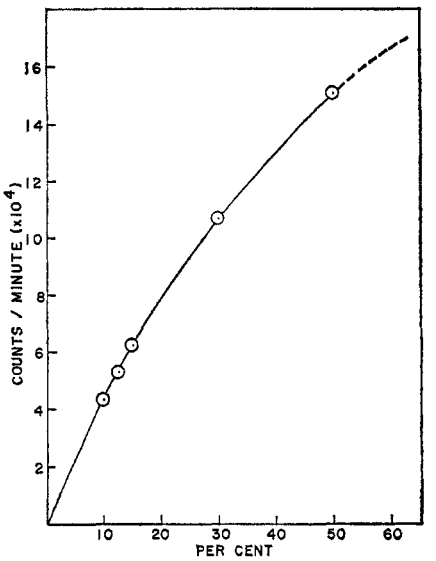

Figure 2. Relationship of activity to concentration of acetrizoic acid over a 50% concentration range

$$S = \sqrt{\frac{N_2}{t_2} + \frac{B}{t_B}}$$

where t_2 is the time of observation of sample plus background and t_B is the time of observation of background. Thus, for the counting times described, the standard deviation was

$$S = \sqrt{N_2 + \frac{B}{2}}$$

The background counting rate was 4200 c.p.m. Thus the 10% solution, which gave a net counting rate of $N_1 = 43{,}465$ c.p.m., had a standard deviation of ±223 c.p.m. or ±0.51%. Similarly, for the 50% solution, where $N_1 = 150{,}688$ c.p.m., the standard deviation was ±396 c.p.m. or 0.26%.

Since the percentage counting error decreases with increased counting rates, using large volumes for activation greatly improves the precision of the activation analysis technique. Conventional methods of activation analysis using volumes of 5 ml. would result in counting rates at least 200 times less because of the small sample sizes involved. The estimated precision resulting for this situation would be ±6.8% for the 10% solution and ±3.97% for the 50% solution using irradiation and counting times identical to those described.

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Identification of Ions in High Resolution Mass Spectrometry by Use of Doublet Mass Differences

SIR: High resolution mass spectrometry, used to an increasing extent for structural diagnostic work, requires accurate determination of ion masses to obtain their composition. Earlier workers (*2*) in examining complex petroleum fractions have used hydrocarbon ions occurring in the high resolution mass spectra as internal mass references for these determinations. These authors measure the mass difference between an unknown ion and a reference hydrocarbon ion; from this difference, they are able to deduce the composition of the unknown in terms of both its hydrocarbon and heteroatom portions. Experience gained in our laboratories has led to the development of a simple graphical method for obtaining ion compositions from the mass differences of doublets derived from accurately measured mass ratios. This procedure has been used with considerable success in the qualitative analysis of many of the complex mixtures encountered in the petroleum industry.

Tables of possible hydrocarbon and heteroatom combinations and corresponding accurate masses, similar to those produced by Beynon (*1*), have been prepared using a computer but because of the large number of possible combinations of elements at any one mass number, these tables have had to be restricted to a small number of elements. Although tables of heteroatom/-hydrocarbon doublets with the corresponding values of ΔM have been drawn up, graphical presentation of ΔM values facilitates the choice of possibilities for a measured doublet. Graphical presentation can be obtained by calculating and plotting ΔM values but a simpler method of setting up the graphs for any combination of heteroatoms has been devised. This method permits a wide range of doublets to be considered without tedious calculation and a rapid assignment of empirical formulas to the peaks in a mass spectrum may be made. The resolving power, $\Delta M/M$, required to resolve a particular doublet can also be quickly estimated.

This simple graphical method has been used satisfactorily in the rapid detection of the nonhydrocarbon constituents, such as sulfur and oxygen compounds, in petroleum fractions (*4*).

Table I. Doublets of the N, N_2, and S Series

Doublet	ΔM
N-H_{14}	0.106
N-CH_2	0.013
N-C_2H_{-10}	0.081
N-C_3H_{-22}	0.175
N_2-CH_{16}	0.119
N_2-C_2H_4	0.026
N_2-C_3H_{-8}	0.069
N_2-C_4H_{-20}	0.163
S-C_2H_8	0.091
S-C_3H_{-4}	0.003
S-C_4H_{-16}	0.097

THEORETICAL

Graphical Presentation of ΔM Values. The ΔM values of the doublets in Table I were plotted as ordinate and the carbon number involved in the doublet as abscissa, Figure 1. A doublet series—e.g., N-H_{14} (carbon number 0), N-CH_2 (carbon number 1), N-C_2H_{-10} (carbon number 2), etc.—lies on a V-shaped line which is parallel to the lines of

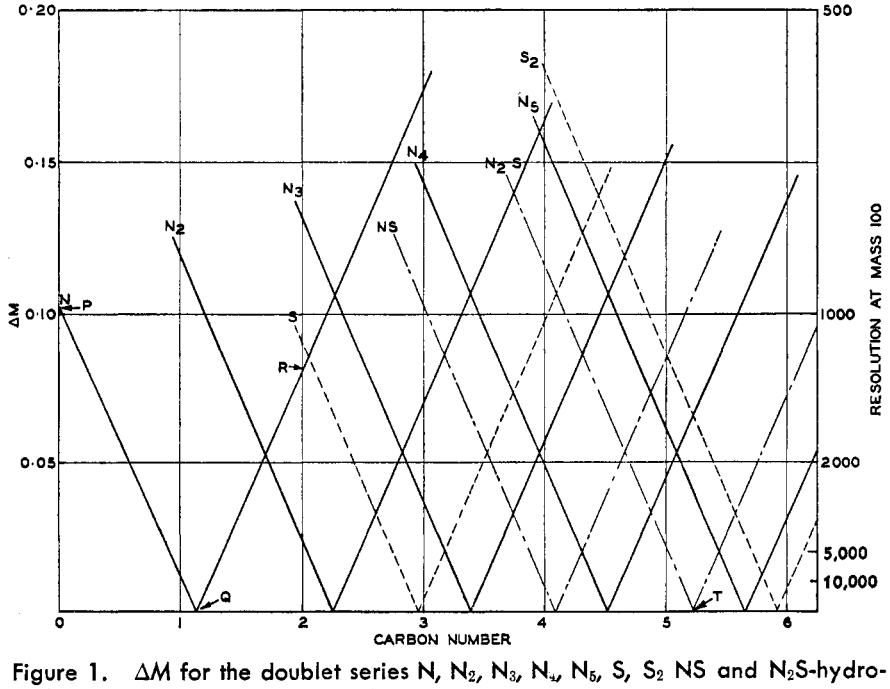

Figure 1. ΔM for the doublet series N, N_2, N_3, N_4, N_5, S, S_2 NS and N_2S-hydrocarbon