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FLUORESCENCE EFFECTS IN ION EXCHANGE RESINS

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MINERAL SCIENCES DIVISION

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FLUORESCENCE EFFECTS IN ION EXCHANGE RESINS

by

T.R. Flint^{*} and G.G. Eichholz^{**}

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SYNOPSIS

Fluorescence under ultraviolet illumination has been observed in anion and cation exchange resins when in the unloaded state. This fluorescence decreases rapidly in intensity as the resin is loaded and this process has been shown to offer a practical method for controlling the loading and elution cycles in ion exchange operations.

The relative effectiveness of different resins and various ions on this fluorescence quenching process has been determined and some correlation has been found between quenching efficiency and ionization potential of the elements. The measurements have shown adequate stability and reproducibility for industrial control applications.

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Direction des mines

Rapport de recherches R 91

EFFETS DE FLUORESCENCE AU SEIN DES RÉSINES
ÉCHANGEUSES D'IONS

par

T. R. Flint* et G. G. Eichholz**

RÉSUMÉ

Les auteurs ont observé la fluorescence à la lumière ultraviolette dans le cas de résines échangeuses d'anions et de cations non saturées. L'intensité de cette fluorescence diminue rapidement à mesure que la résine se sature, et l'on s'est rendu compte que cette technique permet de régler les cycles de saturation et d'élution au cours des opérations d'échange ionique.

On a déterminé l'efficacité relative de différentes résines et de différents ions sur ce procédé d'extinction de la fluorescence, et l'on a établi une certaine corrélation entre l'efficacité d'extinction et le potentiel d'ionisation des éléments. Le dépouillement de ces mesures a révélé une stabilité suffisante et la possibilité d'y recourir pour les applications industrielles de vérification.

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INTRODUCTION

Ion exchange processes are being used to an increasing extent for chemical separation and extraction in the metallurgical industry. To a large extent this widespread use has followed the development of synthetic ion exchange resins which have greatly expanded the possible operating conditions and extraction yields as compared with those obtainable with natural mineral exchange materials (1, 2). The choice of operating conditions and the possibility of control of ion exchange columns have always been fairly limited. In some processes visible colour changes or specific indicators may be used to show the location and extraction of selected ions in the resin column. In the case of natural radioactive ions, fission products or labelled ions, an external counter may be used to record the progress of the reaction; more recently scintillating materials have been introduced into the resin for this purpose(3). In most cases, however, direct control of loading and eluting conditions in the resin has been difficult or impractical, and loading, breakthrough and saturation conditions have had to be inferred from analyses of the effluent solutions. This procedure introduces inevitable time lags and does not readily lend itself to direct control of ion exchange column operations.

Early in 1959, A.J. Gilmore observed (4, 5) that there is a marked change in the fluorescence of some anion exchange resins

excited by ultraviolet radiation as they react with uranyl sulphate complex ions. Originally he had intended to use the well-known fluorescence of uranium salts as a measure of the amount of uranium adsorbed on the resin; instead he found that the unloaded resin fluoresced much more strongly than the resin did after adsorbing varying amounts of uranyl (UO_2^{++}) ions in the form of the uranyl sulphate complex. Following this discovery, an extensive series of tests was done to elucidate this phenomenon and to investigate its possible application to the control and observation of loading conditions for several anion and cation resins when used to extract a variety of ions of practical interest. This report is a summary of this work.

Ion exchange resin processes involve the reaction of one or more ions in solution with the active radicals of an ion exchange resin, followed by selective regeneration of the original resin. Most of the cation resins are synthetic polymers containing free sulphonic acid groups. The anion resins usually contain quaternary ammonium groups with replaceable hydroxyl groups. Unfortunately, it has proved very difficult to obtain much more precise information on the structure and composition of the resins. The distribution of any ionic species between a solution and the resin depends on the composition, pH, and temperature of the solution. Only a certain fraction of the ions in the solution reacts with the resin under equilibrium conditions; the remainder will pass through the column

and appear in the effluent. As the exchange reaction progresses down a column, after the pregnant solution is admitted from the top, efficient and economic operation of the column depends on precise control of solution flow; the incoming solution should be shut off as soon as the resin at the bottom of the bed or column has reached equilibrium with the desired ion ("saturation condition"), since any further ions would merely pass through the column ("breakthrough condition") and would thus be lost to the subsequent recovery cycle. The ions are recovered by stripping them from the resin by means of a suitable acid eluant or by an eluant solution containing an appropriate complexing agent. Again, it is highly desirable to be able to control the elution cycle by obtaining an indication of the completion of stripping of the ions from the resin. The tests performed so far have shown that, under favourable conditions, fluorescence of the resin may be a useful tool to indicate the existence of saturated or unloaded conditions.

Under actual operating conditions, breakthrough may start before full saturation of the resin has occurred. As an arbitrary criterion at the Mines Branch laboratories, breakthrough is assumed to occur when the effluent concentration exceeds more than one per cent of the ion to be exchanged contained in the pregnant solution. This breakthrough is established much more readily by an observation of the fluorescence of the resin.

EQUIPMENT AND TEST PROCEDURE

The equipment required to study the fluorescent behaviour of ion exchange resins has been kept as simple as possible. A Pen-Ray mercury-quartz lamp has been used as the light source and a photomultiplier tube, DuMont type 6365, has been used as the detector, in conjunction with the necessary amplifier and recorder units. Filters were used to minimize the pick-up of scattered and reflected light from the light source.

The batch-test fluorimeter has been provided with a "V" type iris to permit adjustment of the source intensity to a standard value. An ultraviolet pass filter (Corning No. 7-51) was placed between the lamp and the resin sample, and a visible-pass filter (Corning No. 3-72) between the resin and the photomultiplier tube, to reduce reflected background. This filter combination passed a small amount of red light, which could still be picked up by the detector, but its intensity was considered low enough to be neglected.

Fig. 1 is a diagram of the initial test system. Fig. 2 shows a photograph of a later unit made up for batch tests on various resins and solutions. Cyclic tests were carried out to observe reproducibility and possible fatigue of the resin, by recording the fluorescence curves from a 100 ml column taken through a large number of loading-elution cycles. This was done with the equipment

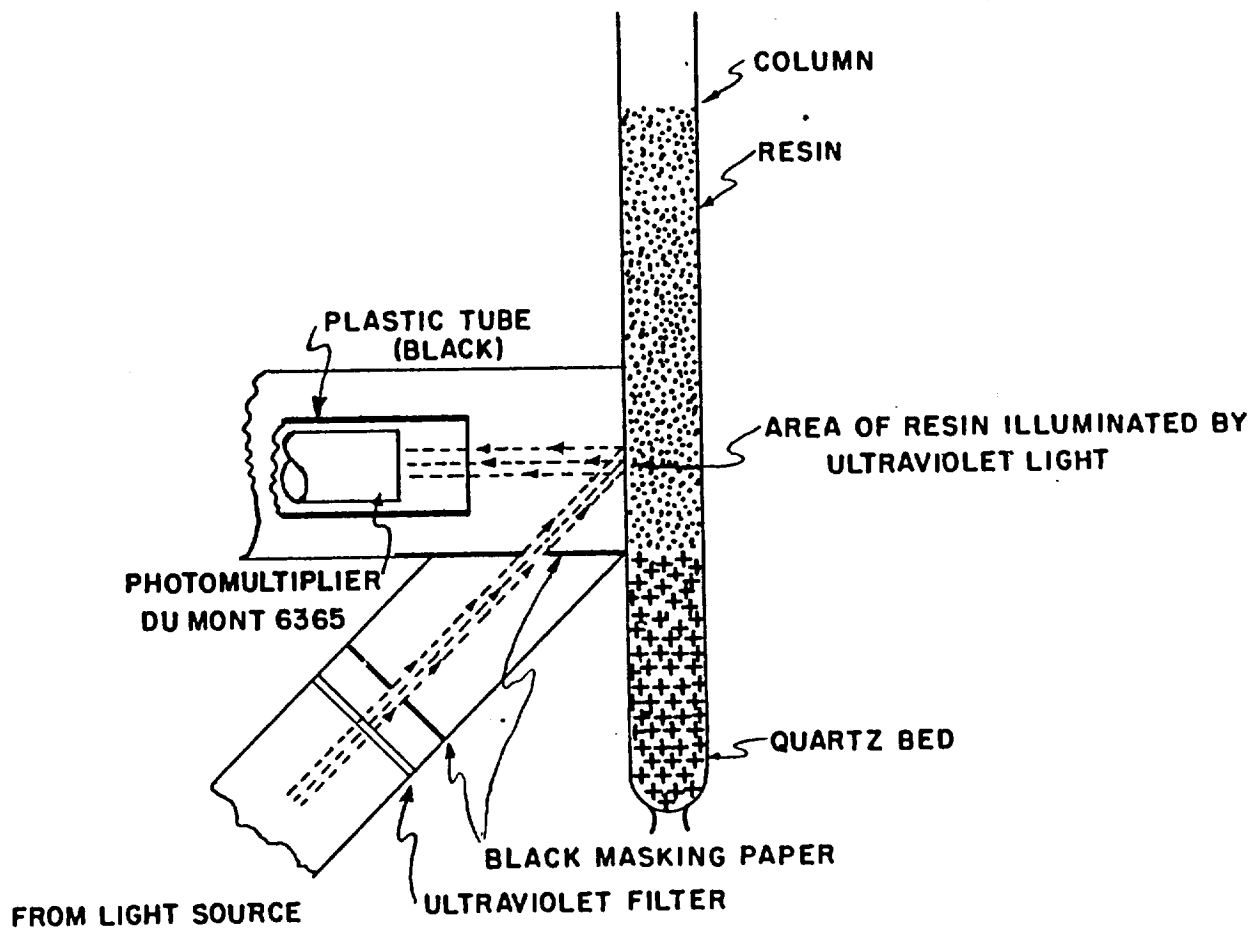


FIGURE I DIAGRAM OF EXPERIMENTAL ARRANGEMENT.

EQUIPMENT AND TEST PROCEDURE

The equipment required to study the

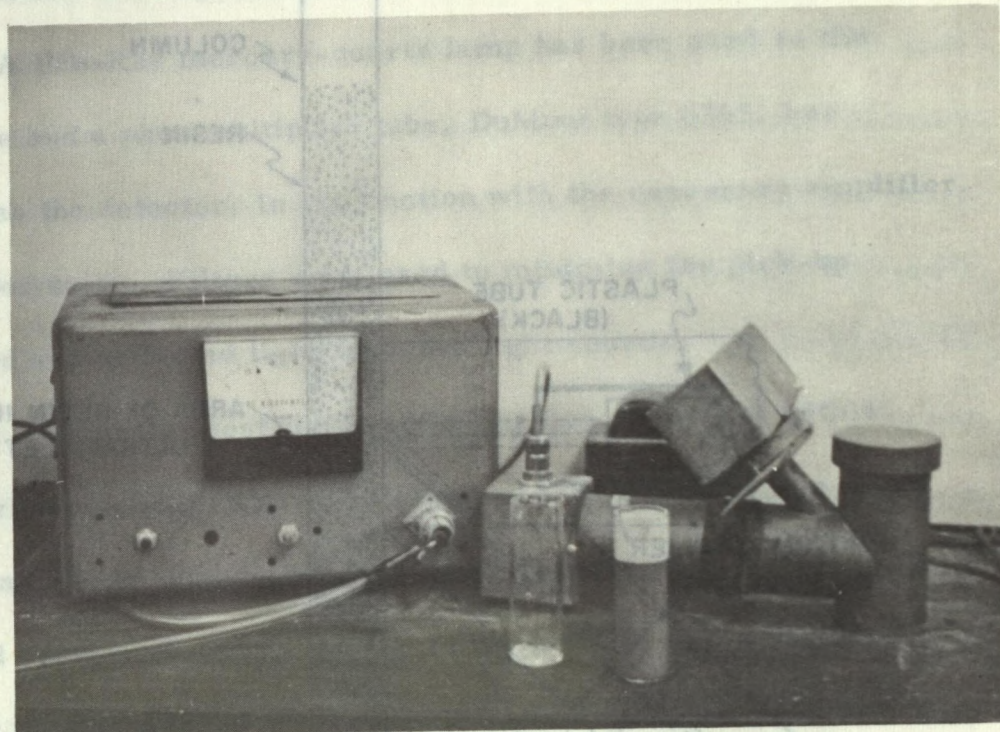


Figure 2 - Batch Test Unit

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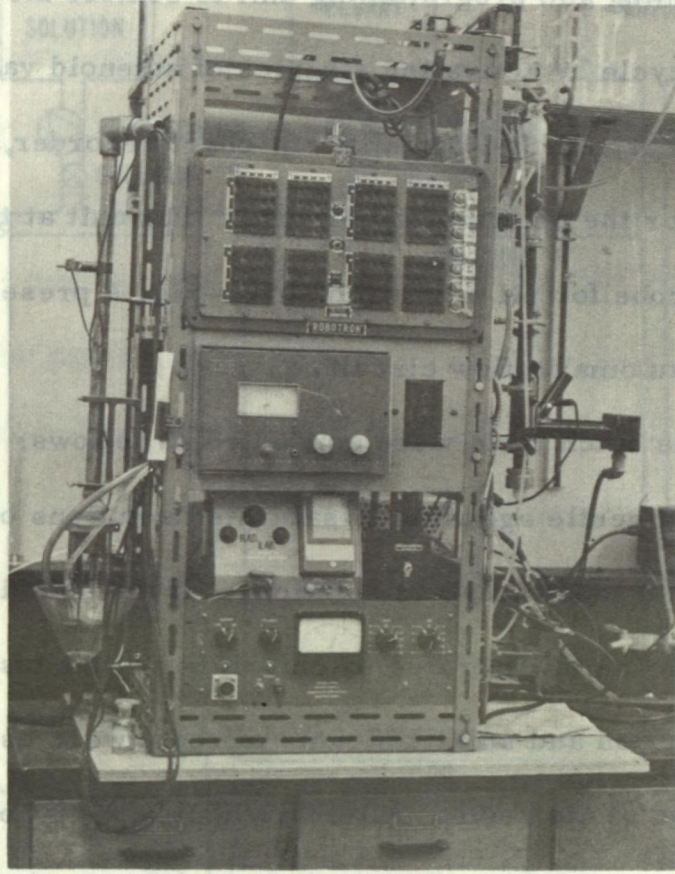


Figure 3 - Automatic Cycling Test System

shown in Fig. 3 which contains the resin column, protected from daylight and with the fluorescence unit attached, at the right of the framework. The framework itself supports, from top to bottom, a "Robotron" timer and programming unit to control the successive phases of each cycle. The Beckman pH meter, a voltage supply for the Beckman pH meter, a sampling probe for the diagram of the amount of the resin, a fresh resin was placed under the appropriate ion appropriate ion appropriate salt was quantities of solution ensure saturation resin was rinsed in distilled water to avoid light absorption by the solution. The cell was then measured by means of the fluorimeter. After measuring the fluorescence, the resin was eluted with HCl and the eluant analysed chemically for presence of the metal ion.

FIGURE 4 AUTOMATIC FLOW CIRCUIT.

For the continuous flow tests, the change in fluorescence intensity was recorded as the sample solution passed through the column, and as the column was successively washed, loaded, eluted and regenerated. Two solutions were tested, a uranyl sulphate

shown in Fig. 3, which contains the resin column, protected from daylight and with the fluorescence unit attached, at the right of the framework. The framework itself supports, from top to bottom, a "Robotron" timing and programming unit to control the successive phases of each cycle by activating a series of solenoid valves, a Beckman pH meter, a YSI-Rustrak strip-chart recorder, and a high-voltage supply for the photomultiplier tube. The unit at the left is a sampling probe for pH measurements. Fig. 4 presents a diagram of the automatic flow circuit.

The batch tests were conducted as follows: Fresh resin was placed under gentle agitation in saturated solutions of the appropriate ion, usually sulphate solutions. If the solubility of the sulphate salt was too low, nitrates or chlorides were chosen. Large quantities of solution and small amounts of resin were used to ensure saturation of the resin. After one hour's agitation the resin was rinsed in distilled water to avoid light absorption by the solution. The fluorescence intensity of the resin in the quartz cell was then measured by means of the fluorimeter. After measuring the fluorescence, the resin was eluted with HCl and the eluant analysed chemically for presence of the metal ion.

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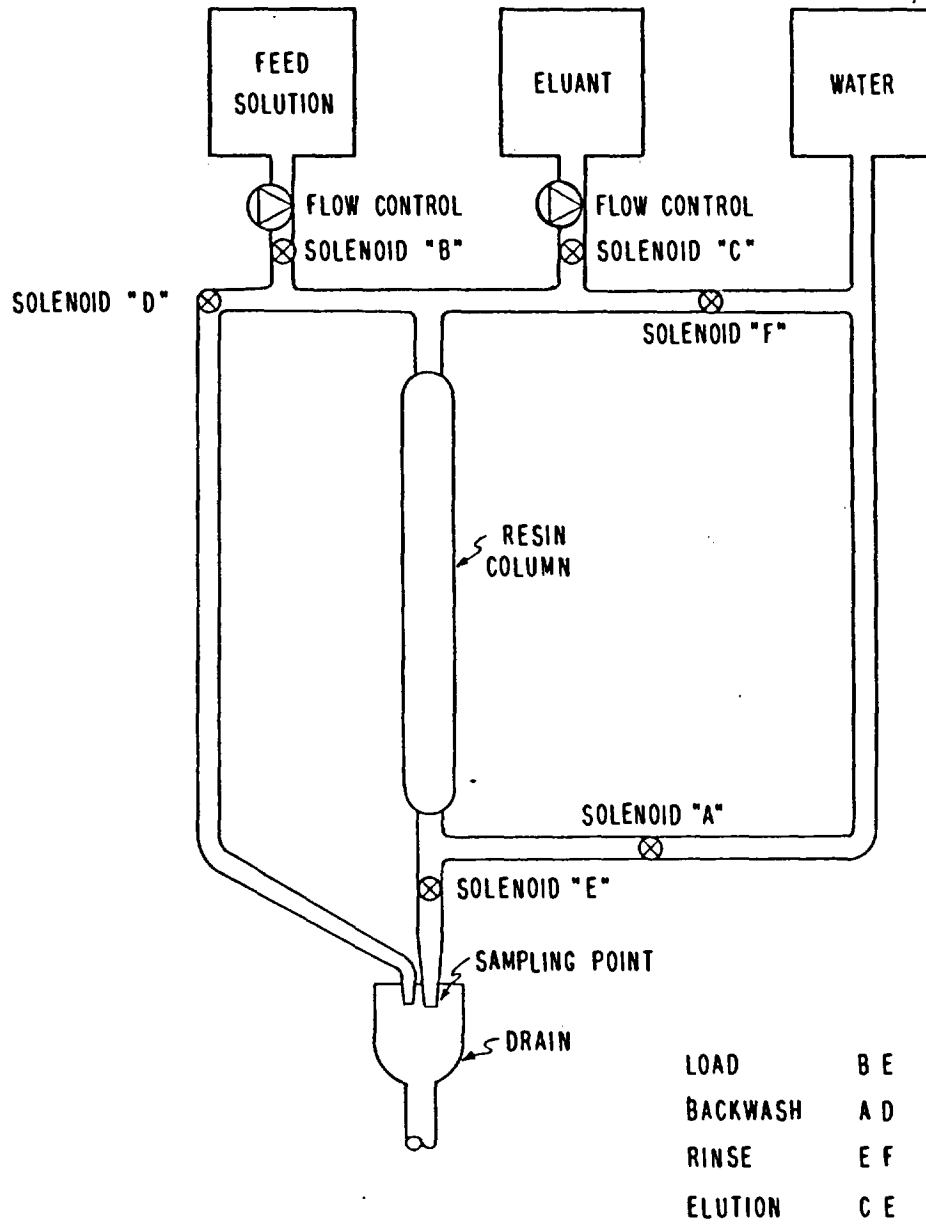


FIGURE 4 AUTOMATIC FLOW CIRCUIT.

solution, 2 g/l, buffered to pH 1.5 with MgSO_4 and held to a minimum of 30 g/l $\text{SO}_4^{=}$ ion with H_2SO_4 , and a ferric sulphate solution (1 g/l) maintained in an acid condition with 30 g/l H_2SO_4 .

For these column tests, a lime-glass column was used. Two types of resins, Amberlite IR-120 and IRA-400, were tested by means of cycling operations with ions that had been shown by batch tests to be effective; i.e., the resins displayed large variations in fluorescence on passing from the fresh to the loaded condition. Concentrations in the pregnant solution were adjusted so that the column would load in a reasonable time. The equipment was then allowed to run continuously, for several days at a time, until several dozen full cycles were completed. The strip-chart recordings of the fluorescence output were then compared with chemical assay results of samples taken at a number of selected points in the sequence, in order to establish a correlation between resin fluorescence and effluent assays. The chemical results showed a fixed lag of about 50 ml as compared with salient points on the graph. Much of this lag is accounted for by the difference in the location of the portion of the resin column viewed by the fluorescence unit and the location of the sampling container used to collect the effluent liquid at the foot of the column. A correction for this lag could be made in controlling a process.

RESULTS OF FLUORESCENCE TESTS

1. Anion Exchange Resin Tests

Since the original impetus for this investigation arose from the extraction test work at the Mines Branch laboratories on uranium-bearing solutions using anion resins, much of the preliminary work was concerned with such solutions.

In anion exchange, uranium is complexed and adsorbed as the uranyl sulphate complex ion. Both batch tests and continuous runs were conducted using synthetic sulphuric acid solutions, containing 0.87 g U_3O_8 /l, and some pregnant mill solutions containing comparable amounts of uranium. The resin used for these tests was Amberlite IRA-400, a strongly basic anion exchanger of the quaternary ammonium type.

Preliminary batch tests with small amounts of resin and a fluorimeter as a detector had shown that the relation between the amount of uranium adsorbed and the degree of fluorescence quenching is not linear (Fig. 5). Since breakthrough occurs usually before the resin is fully saturated, it was expected that enough variation of fluorescence could be observed over the useful control range of resin operation. This was confirmed in a series of single-cycle qualitative tests in which a galvanometer was used to indicate fluorescent intensity and a Beckman spectrophotometer

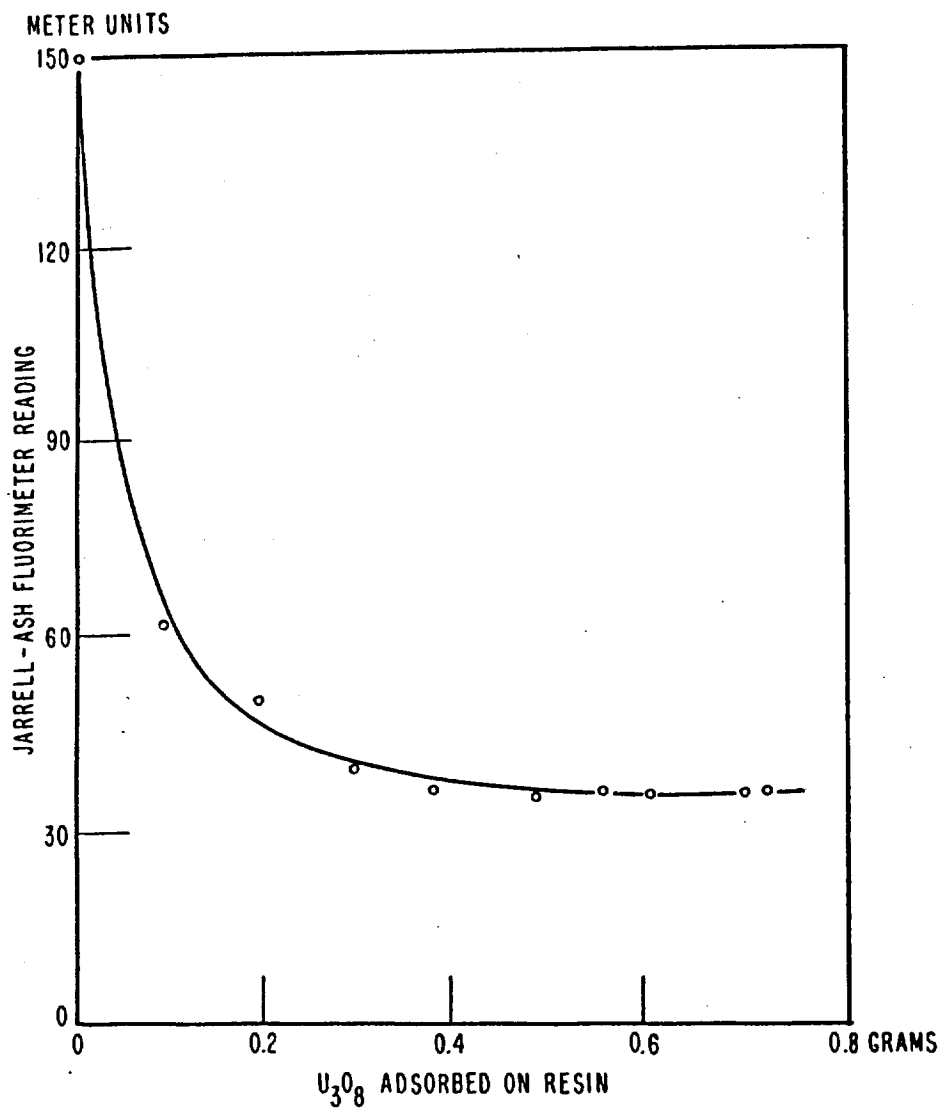


FIGURE 5 FLUORESCENCE CURVE FOR RESIN LOADING.
10 ml AMBERLITE IRA-400 RESIN

was used for rapid colorimetric indication of the uranium content of the effluent solutions. Fig. 6 presents the results for a synthetic uranium sulphate solution (0.87 g U_3O_8 /l) and Amberlite IRA-400 resin. It is seen that there is a considerable change in galvanometer (fluorescence) readings leading up to the uranium breakthrough point. To confirm that the fluorescence quenching was due solely to resin loading, a similar test was performed with a uranium solution to which 0.90 g Fe^{3+} /l had been added. The ferric sulphate complex formed reacts readily with the resin, but is displaced from the resin by the uranyl complex. This situation is illustrated in Fig. 7, which again presents the galvanometer reading of fluorescence intensity and the uranium content in the effluent. It is evident, that loading the resin with the iron complex is sufficient to quench the fluorescence. Replacement of the iron by uranium appears to have little effect on the fluorescence readings. These results were confirmed in tests with typical plant liquors.

After these preliminary tests, long-term cyclic tests were carried out with synthetic uranium solutions. Fig. 8 shows the recorder trace for a typical loading-elution-regeneration cycle. It is seen that the curve shows rather more fluctuations in output than might have been expected. The detector was placed as close to the bottom of the column as possible, so that the large change in

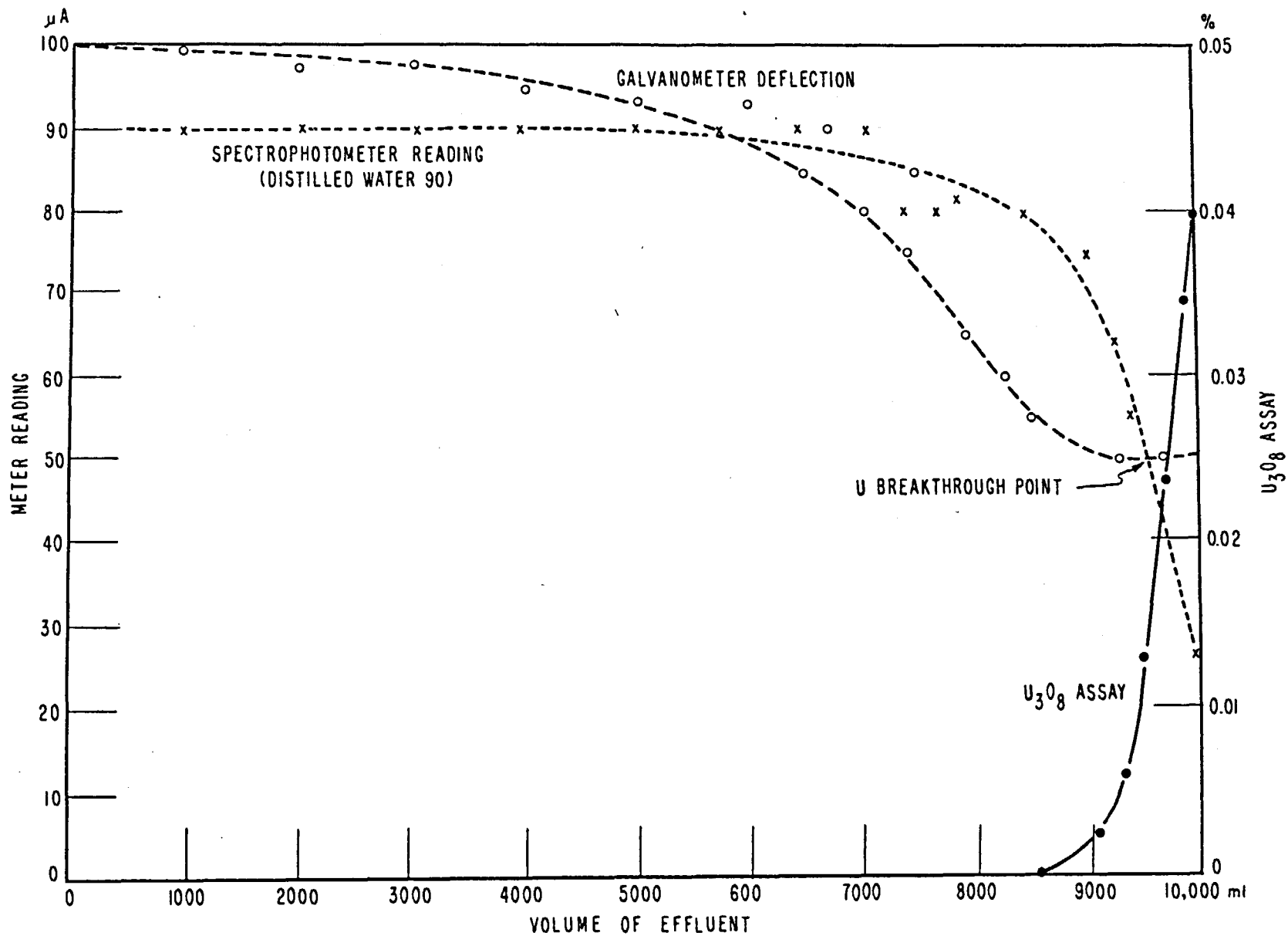


FIGURE 6 FLUORESCENCE CURVE FOR SYNTHETIC URANIUM SOLUTION.

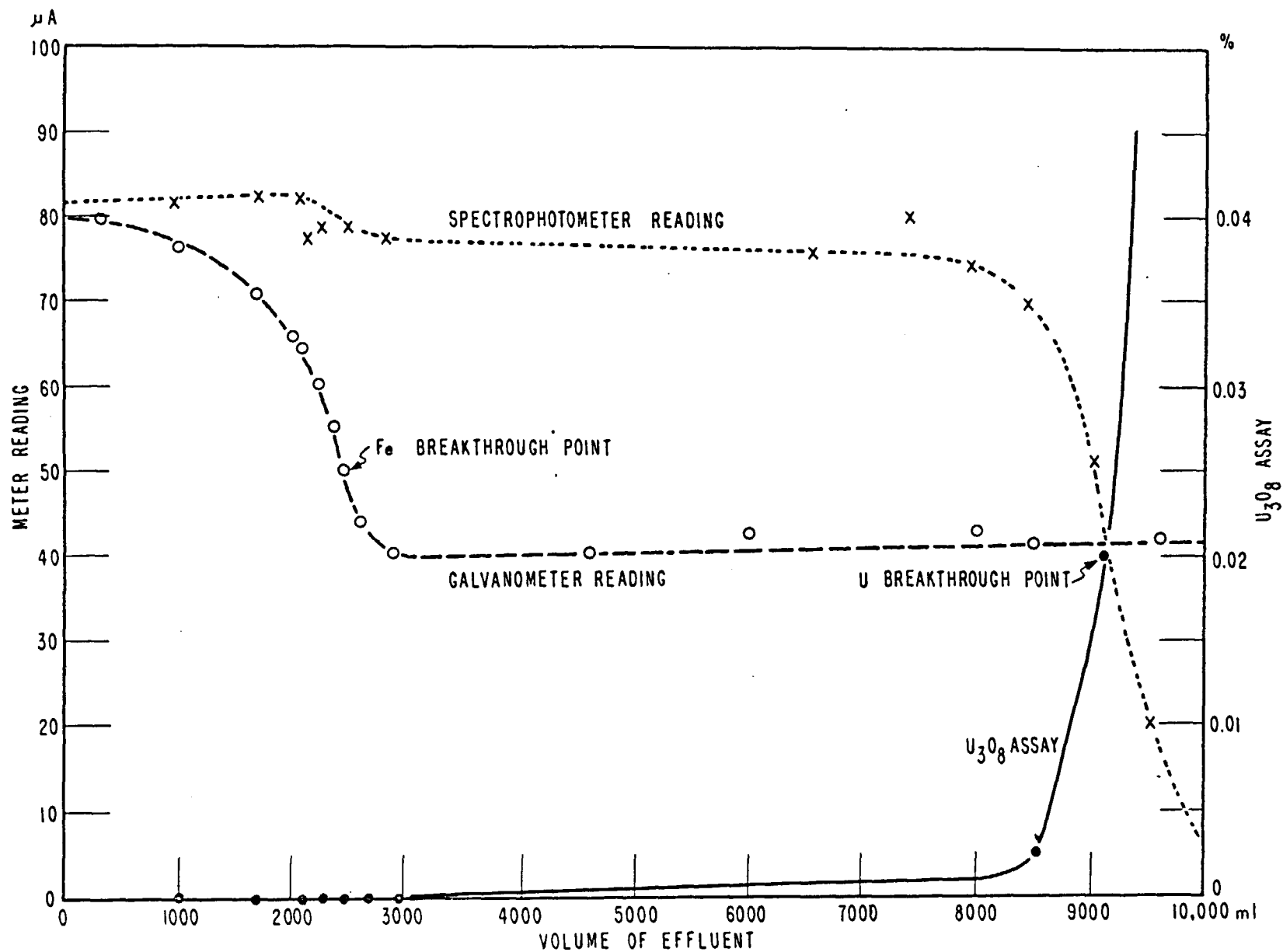


FIGURE 7 FLOURESCENCE CURVE FOR SYNTHETIC URANIUM SOLUTION WITH Fe^{+3} ADDED.

FLUORESCENCE INCREASE

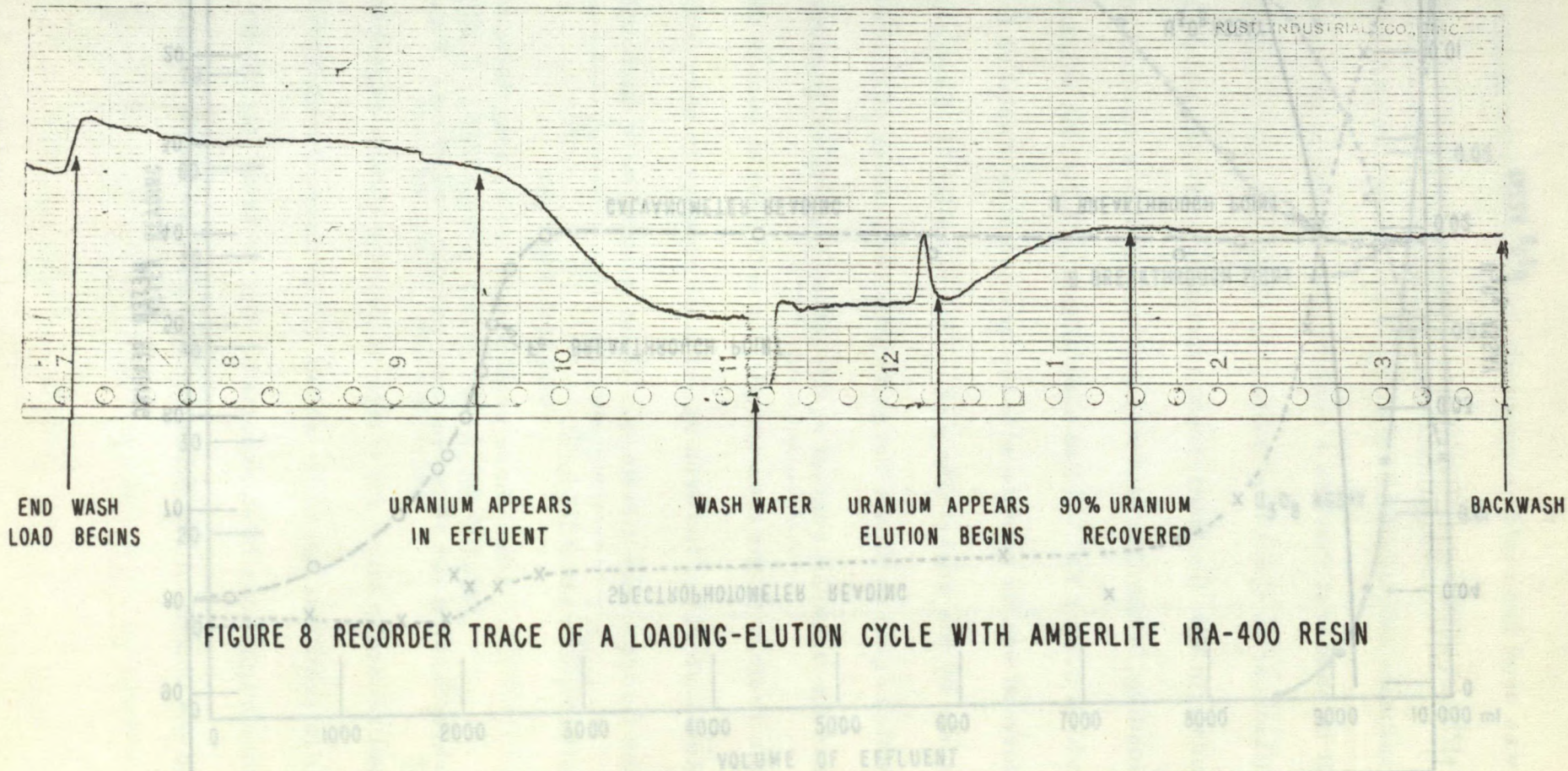


FIGURE 8 RECORDER TRACE OF A LOADING-ELUTION CYCLE WITH AMBERLITE IRA-400 RESIN

FIGURE 6 FLUORESCENCE CURVE FOR SYNTHETIC URANIUM SOLUTION

fluorescence intensity is followed almost immediately by uranium breakthrough. The major discontinuity during elution with HCl seems to be clearly associated with the replacement of the uranyl sulphate ion on the resin by chloride ions. This discontinuity is shown in more detail in Fig. 9, which contains an analysis of the elution phase of the cycle in terms of fluorescence, pH readings and of the uranium content of the eluant. The correlation between these readings is evident, particularly when the fluorescence curves are shifted (dotted to solid curve) to allow for the dead volume at the bottom of the column.

The reproducibility of all these results was remarkably good. The gross changes in fluorescent intensity were of the order of 30 - 80% of the maximum reading. Fluctuations from run to run in a total of several hundred runs amounted only to about 10% in the magnitude of these changes. In the case of the anion exchange tests, an overall fluctuation of 8% was observed in the range of output readings that would be of interest in control applications. In view of the abruptness of the changes in fluorescence output, such 8% fluctuations would be of relatively minor importance.

It was also observed that intense ultraviolet illumination appears to bleach the resin. It was noted that the fluorescence increases slowly if the resin is left in the loaded condition while being illuminated. In this case the uranium could not be eluted

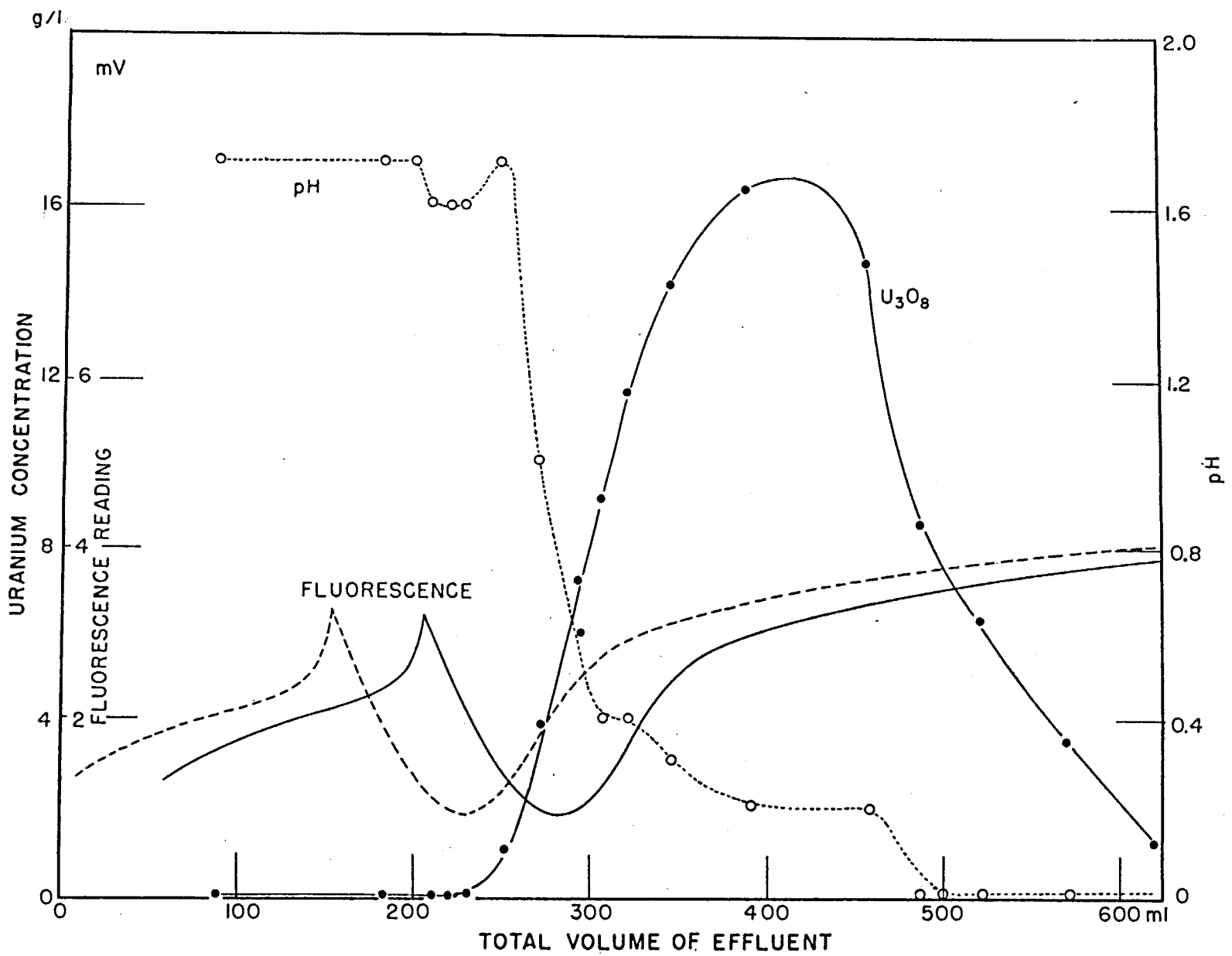


FIGURE 9 PLOT OF VARIABLES IN ELUTION CYCLE:
URANIUM EXTRACTION BY ANION RESIN.

FLUORESCENCE - AS MEASURED----- , CORRECTED FOR DEAD VOLUME (50 ml) —

properly from the exposed grains and it would seem that a secondary reaction takes place between the uranyl sulphate ion and the resin. It is known, that the uranyl ion, UO_2^{++} , is photochemically very active and may promote ultraviolet radiation decomposition of the organic resin, though this effect has not been observed in the present work. In any case, it is of little practical importance because the movement of the resin bed during backwashing would expose different grains to the illumination in every new cycle.

2. Cation Exchange Resin Tests

A number of cation exchange resins were tested under conditions similar to those used for testing the anion resins. It was soon evident that in this case marked fluorescence quenching can only be expected if there is a marked change in the vibration damping of the resin from the "fresh" condition, with a hydrogen ion attached to the active group, to the "loaded" condition, with any other cation replacing hydrogen. The effect was fairly easily observed with a ferric sulphate solution; Fig. 10 shows a recorder trace of a typical cycle for Fe^{+3} loading and HCl elution for Amberlite IR-120 resin, a strongly acidic cation exchanger. Again, good correlation was obtained between the fluorescence readings and chemical assays of the effluent solution.

Various types of resin were tested to establish the magnitude of the fluorescence effect. Table 1 lists the results of batch tests with saturated solutions, for both cation and anion resins for comparison. The "per cent quench"

figure is defined as the ratio of the difference reading between unloaded and loaded resin to the reading for the unloaded resin (after subtracting the dark current), times 100.

TABLE 1

Comparison of Fluorescence Effect on Various Resins

Trade Name	Structure and Active Groups	Adsorbed Ion	Per Cent Quench
Amberlite IR-120	Cation exchanger, strongly acidic, cross-linked polystyrene	Fe^{+3}	80
Permutit Q	"	Fe^{+3}	26
Permutit SK	Anion exchanger, highly basic quaternary amine	ferric sulphate complex	19
Amberlite IRA-400	Strongly basic anion exchanger, quaternary ammonium polystyrene	U-complex	30
Deacidite	Anion exchanger, weakly basic aliphatic amine	Cl^{-}	31

The results of Table 1 reflect the variation in structure of the resins made by different manufacturers and possibly, also, some variation in resin purity. They all show measurable changes in fluorescence quenching with loading.

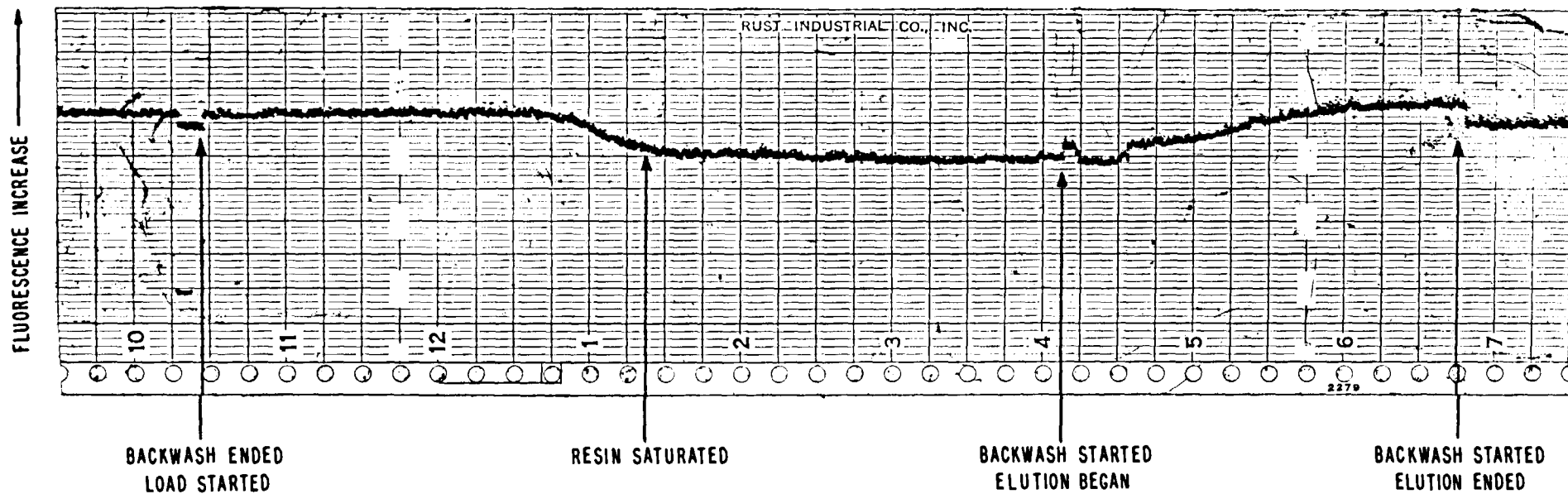


FIGURE 10 RECORDER TRACE OF A LOADING-ELUTION TEST WITH AMBERLITE IR-120 CATION RESIN
 $\text{Fe}_2(\text{SO}_4)_3$ LOADING-2 N HCl ELUTION

To determine the relative effectiveness of different ions on the quenching of resin fluorescence, batch tests were done with Amberlite IR-120 resin for a number of the more important ions. The results of these tests are collected in Table 2, together with a list of the ionization potentials of the elements as referred to hydrogen (6). It is seen that there appears to be a rough correlation between the net fluorimeter reading and the relative ionization potential. This is shown graphically in Fig. 11. The ionization potential is probably of significance here as an indication of the bond energy between the active group in the resin and the adsorbed ion; similar correlation may be obtained with the lyotropic series of ions (7). The discrepancy observed in the case of cerium suggests that it is exchanged as a complex rather than a simple Ce^{3+} ion; a similar consideration applies to the $\text{Al}_2(\text{SO}_4)_3$ solution listed in Table 2.

It is evident that observations on fluorescence intensities alone may not be sufficient to identify the particular ionic species exchanged or displaced if ions of comparable quenching efficiency displace each other on the resin.

TABLE 2

Cation Adsorption on Amberlite IR-120 Resin

Ion	Fluorimeter Reading			Quench (%)	Ionization Potentials (eV)	Rel. Ionization Potential (difference from H+) (eV)
	Fresh H+ Resin (μA)	Loaded Resin (μA)	Difference (μA)			
H ⁺					13.53	-
Na ⁺	68	68	0	0	5.12	-8.41
Mg ⁺⁺	68	68	0	0	14.96	+1.43
Pb ⁺⁺	68	64	-4	5.9	14.96	+1.43
Cd ⁺⁺	68	66	-2	2.9	16.84	3.31
Co ⁺⁺	68	50	-18	26.5	17.3	3.77
Hg ⁺⁺	68	58	-10	14.5	18.65	5.12
Cu ⁺⁺	68	54	-14	20.5	20.34	6.81
Ce ⁺⁺⁺	50	49	-1	2.0	~ 24	+10.5
Fe ⁺⁺⁺	68	14	-54	79.5	~ 35	21.5
(UO ₂) ⁺⁺ in uranyl sulphate complex	70	59	-11	17.2		
Al ₂ (SO ₄) ₃ solution	50	52	+2			

Normal dark current: 6 μA
 Water reflectance: 20 μA
 Empty cell: 8 μA

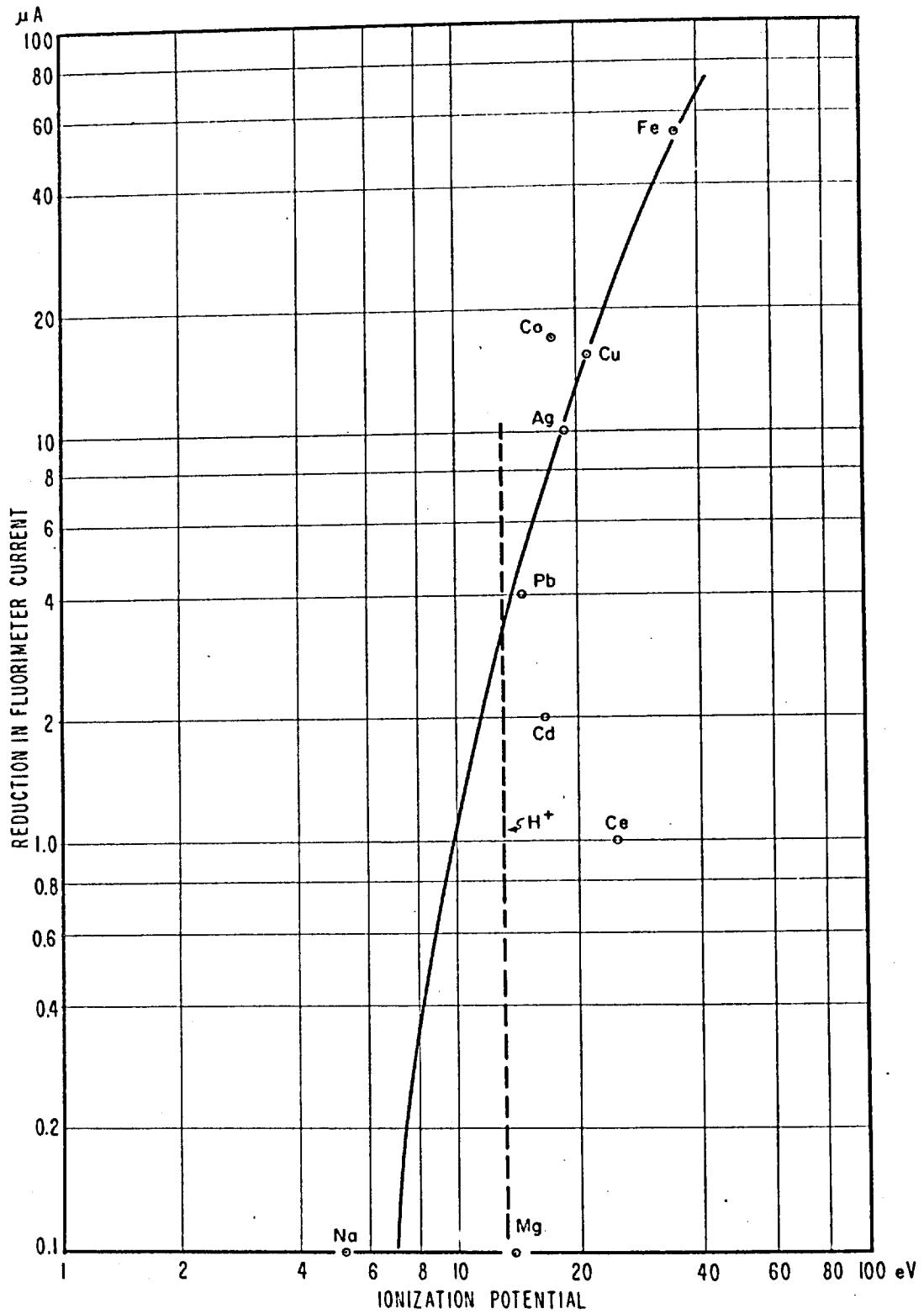


FIGURE II RELATION BETWEEN FLUORESCENCE QUENCHING AND IONIZATION POTENTIALS.

3. Spectrographic Tests

Before ascribing the reduction in fluorimeter reading to simple quenching of the principal molecular excitation states in the resin molecule, it was considered worthwhile to determine if the observed intensity changes could be due to a shift in the spectrum distribution of the fluorescence as exchange takes place in the resin. Since the photomultiplier tube has an S-11 response peaked at 4400 A, a major shift in the emitted spectrum distribution would appear to result in a reduction in the output reading. Such shifts would be of little interest in industrial processes, but might find some practical application in analytical problems.

A Beckman recording spectrophotometer with fluorescence attachment was used to obtain the fluorescence spectra of IR-120 resin in various states when excited by narrow band radiation from a monochromator. Two bands, mercury lines at 3650 A and 2537 A, were used for excitation and wet resins loaded with hydrogen, cerium, cadmium and ferric ions, respectively, were examined. Figures 12 and 13 show the smoothed and normalized fluorescence distribution for the various resin states when excited with 3650 A and 2537 A respectively, and Fig. 14 is the manufacturer's spectral response curve for the photomultiplier used.

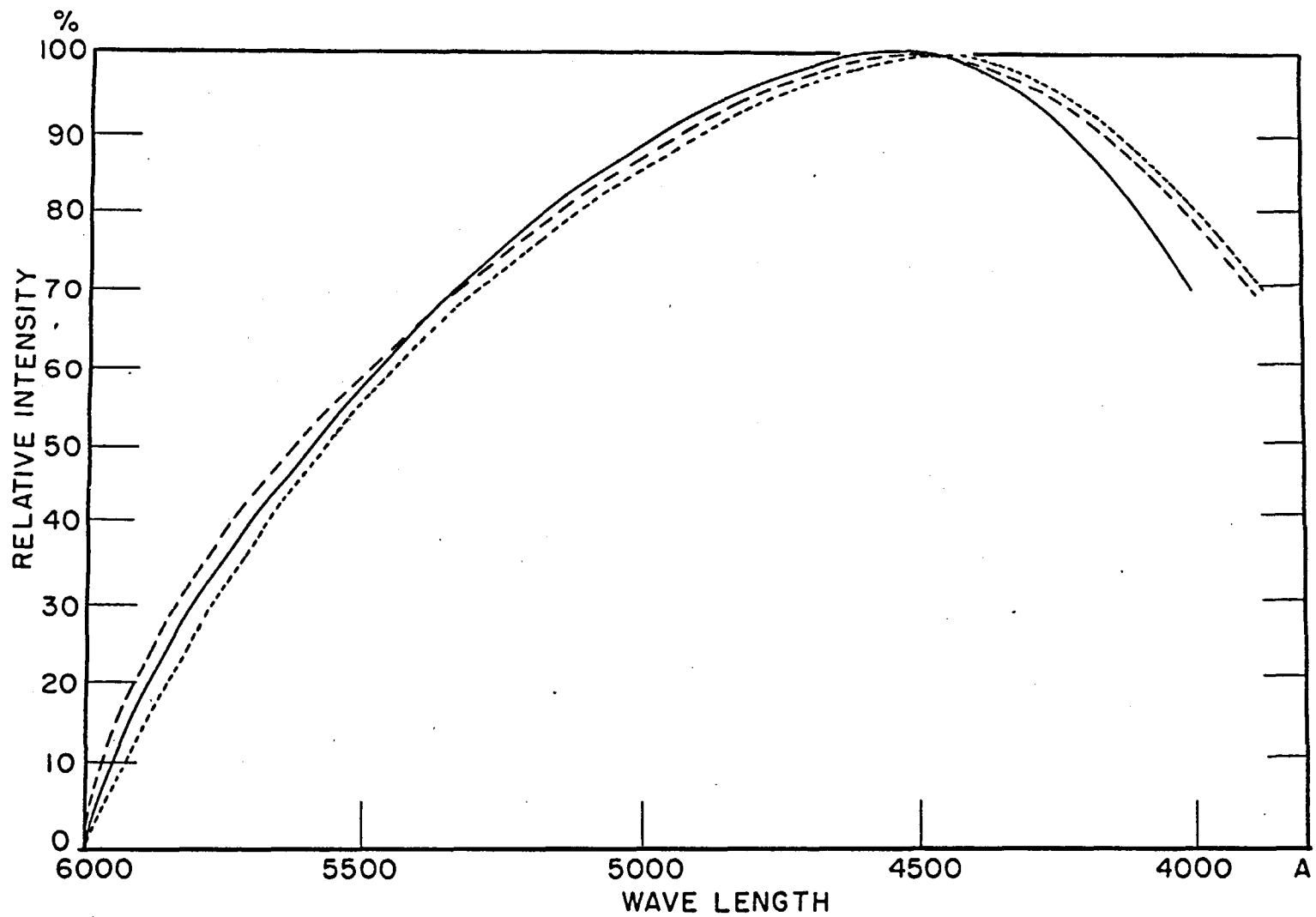


FIGURE 12 FLUORESCENCE SPECTRA OF IR120 RESIN: EXCITATION WAVE LENGTH 3650A.

FRESH RESIN Cd LOADING ——— Ce LOADING - - - -

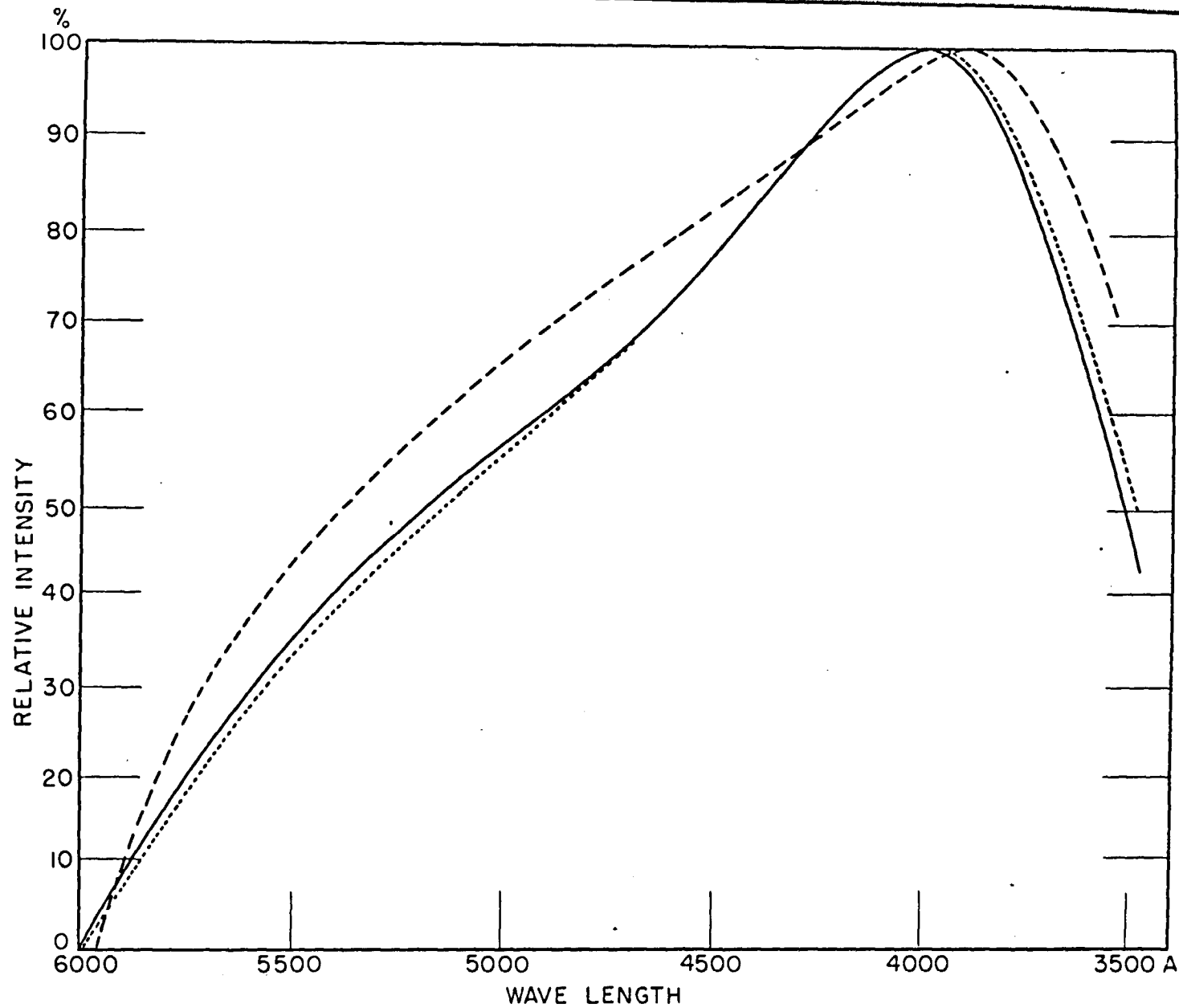


FIGURE 13 FLUORESCENCE SPECTRA OF IR 120 RESIN: EXCITATION WAVE LENGTH 2537Å.

FRESH RESIN Cd LOADING ————— Ce LOADING - - - - -

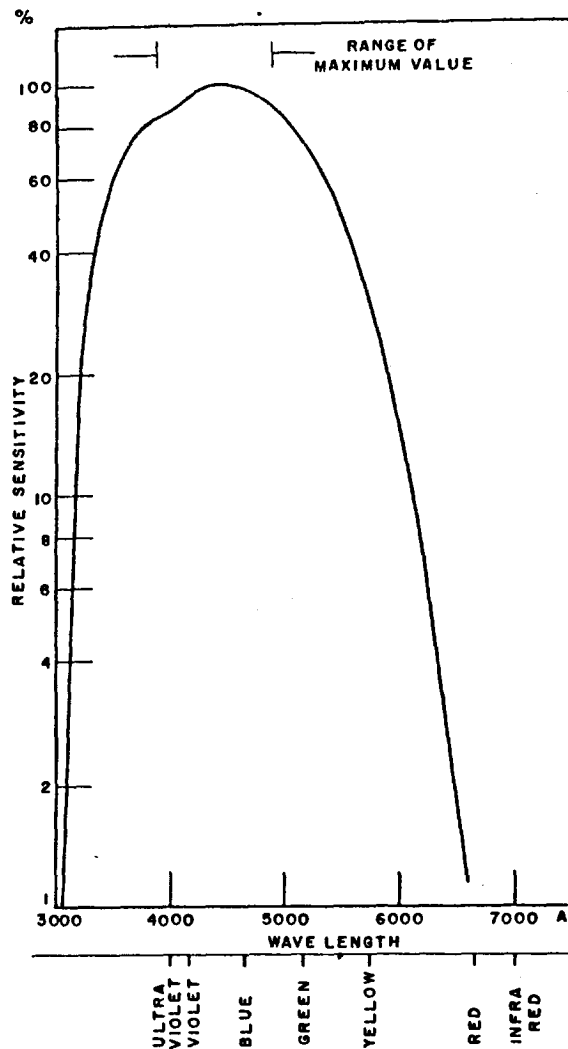


FIGURE 14 SEMI-LOGARITHMIC PRESENTATION OF S-II RESPONSE

The most significant observations from the spectrographic results appear to be as follows:

- 1). There is a broad peak of fluorescence at 4000-4500 A which corresponds to a 3.5-3.2 electron volt transition. One can assume that there must exist a broad band of principal transitions in this region, that moves upward in energy as the excitation energy is increased. It will be noted that there is a 500 A upward shift between the peaks in Fig. 12 and Fig. 13.

This shift is probably due to the increased probability of the existence of higher states of excitation for the higher excitation energy.

- 2) There are slight changes in the position of the peak fluorescence observed for cerium- and cadmium-loaded resin as compared with the peak fluorescence of fresh resin (Figs. 12, 13). This 100 Å shift probably is associated with the increased bond energy of the active bonds that are involved in the reaction between the metal ions and the rest of the polymer.
- 3) It was observed that for Fe^{+3} there is complete quenching of the visible spectrum. It is seen from Table 2, that there is a difference in ionization potential of 21.5 eV between $\dot{\text{F}}\text{e}^{+3}$ and H^{+} ; hence, it is not entirely surprising that a gross change in fluorescence might result from the $\text{H}^{+} \longrightarrow \text{Fe}^{+3}$ exchange reaction.

From the above observations it might be concluded that in the fluorescence of these polymers there is a broad band of principal transition states in the region of 3.2-3.5 eV, and a number of secondary transition states between 2 and 3 eV. These states, however, are very broad overlapping states due to the complex nature of the polymer. The shift of peak fluorescence when the resin is loaded with cerium or cadmium appears to represent the elimination of the higher principal states of excitation

by an increase of total energy in the polymer. The total quenching by Fe^{+3} ions can be interpreted as representing the complete removal of some of the major excitation states below 4 eV (approximately 4000 Å).

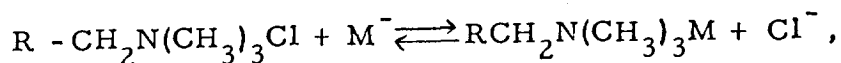
The most likely explanation for the differences observed for the two wavelengths is the probability of excitation of additional energy states in the resin by the shorter wavelength radiation. No assignment of bands is possible in view of the very large number of possible excited states in the resin. The change in peak position with loading of the resin is presumably associated with the preferred quenching of certain molecular vibrations as the exchanged ion is more strongly bound to the resin. Since this attachment does not materially influence the gross structure of the resin and hence its multiplicity of energy states, this effect would have only a minor influence on the observed fluorescence spectrum.

Analysis of Fig. 11 shows that ions which have an ionization state less than 17 eV contribute less than 10% quenching to the resin. This suggests that the principal excitation states are largely located between 3 and 4 electron volts; it further suggests that the quenching of these excitation states is related to the increase in ionization potential of the ion attached to the active bonds of the resin.

DISCUSSION

The work described here should be clearly distinguished from work going on elsewhere on scintillating ion exchange resins (3), in which small amounts of scintillating phosphor reagents are incorporated in the ion exchange resin to indicate the location and concentration of adsorbed radioactive ions. In the present case, we are concerned with the emission of fluorescent light from the resin itself. Most of the ion exchange resins of interest consist of polystyrene units cross-linked to varying degrees with divinyl benzene, with the active groups attached to the main chain. Investigations on plastic scintillation phosphors have shown (8), that polystyrene fluoresces feebly by itself, but that the intensity of fluorescence is greatly enhanced by the addition of suitable phenyl derivatives. In the case of ion exchange resins that are not transparent the observed fluorescence arises presumably from the surface layers only. The difference in intensity of fluorescence between fresh resins, thus depends both on the structure and purity of the resin material itself and on the nature of the active groups. In the case of anion resins, like Amberlite IRA-400, the active group is formed by the treatment with tertiary amine of chloromethyl groups attached to the benzene rings in the polymer. The quaternary reaction taking place then produces the quaternary ammonium chloride group $-\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$. In ion exchange the change from fresh to

loaded conditions involves the reaction



where M is the exchanged ion or ionic complex. If this transition effectively quenches a greater portion of the observed fluorescence-- up to 80%, even allowing for the non-linear relation between detector reading and resin adsorption--it is tempting to ascribe the observed fluorescence to the active group only. However, it is known from fluorescence theory (9), that for a complex molecule the energy band distribution is a function of the molecule as a whole and the effect of changing the bonding energy at the active end of the molecule chain may easily change the energy pattern of the molecule as a whole and hence quench the fluorescence. This behaviour has been found particularly important in phenyl derivatives and applies in the present case.

In the case of cation exchange resins like Amberlite IR-120, the active group is a sulphonic acid radical. The transition from fresh to loaded conditions involves a reaction changing $\text{RSO}_3\text{H} \rightarrow \text{RSO}_3\text{M}$, where M is the exchanged ion. Under conditions of simple exchange of one monatomic ion for another, this may lead to only minor changes in bond energy and would account for the low value of quench efficiency in such cases.

These observations suggest that, for the utilization of fluorescence quenching of ion exchange resins, attention must be paid to the purity and structure of the resin to obtain maximum fluorescence

from the unloaded resin and that one would expect the greatest quenching action if the difference in size and binding energy with the resin between the adsorbed and the displaced ion can be maximized.

CONCLUSIONS

The experiments made indicate that it may be feasible to obtain practical industrial control of continuous ion exchange operations in certain processes by monitoring the fluorescence level of the resin. Some of the applications may involve special techniques, when the fluorescence variations are low, but many of the more important processes could be readily controlled by this method with a consequent improvement in efficiency of operation and reduction of costs. The equipment required would be fairly simple and it is easy to visualize several straightforward methods for installing a monitor of this type.

The fluorescence methods have an additional advantage in providing information on the performance of the resin itself, whereas most other control processes depend on measurements on the effluent solution. Further work on fluorescence effects in such resins can be expected to provide some information on exchange and elution rates, and on purity and other characteristics of the resins themselves. For these reasons the fluorescence method may be

of considerable help in the development of further applications of ion exchange processes in extraction metallurgy and chemical technology.

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