

RECENT ADVANCES IN THE CHEMISTRY OF ORGANOMETALLIC COMPOUNDS OF THE ACTINIDE ELEMENTS

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ABSTRACT

A brief history of the preparation of organometallic compounds (the tricyclopentadienyls) of the 5f-electronic series, the actinides, is presented. The special micro-techniques employed for the heavier actinides, available for investigation in only microgramme quantities, are described. The compounds of the heavier actinides are characterized by largely ionic bonding.

The more recent preparation of cyclooctatetraenyl compounds of the actinides is also described. The uranium(IV) compound is relatively stable, covalent, with a sandwich π -electron structure involving 5f-electrons; since this structure is analogous to ferrocene, the name uranocene has been proposed.

These organometallic compounds are relatively volatile and thus sublime at relatively low temperatures.

The prospect for preparing organometallic compounds of the heaviest actinides and the transactinides, presently available only on a one-atom-at-a-time basis, is also examined on the basis of inorganic chemistry experiments that have already been performed with such small quantities of these and similar elements.

Organometallic chemistry has its origin in the discovery of diethylzinc by Frankland in 1849 and even still earlier work on platinum chemistry performed by the Danish chemist Zeise in 1827. The interest of most transition metal chemists, however, dates from the preparation of ferrocene in 1951. Other d-transition metal 'sandwich' compounds and also compounds of an ionic nature between cyclopentadiene and the 4f-transition metals, the lanthanides, were then prepared. In order to study possible metal to carbon bonding in the 5f-electronic series, the actinides, Reynolds and Wilkinson¹ extended organometallic chemistry to element 92 in 1956 by preparing uranium tricyclopentadienyl chloride, $U(Cp)_3Cl$ (where $Cp = C_5H_5$). The reaction of uranium tetrachloride with sodium cyclopentadienide, $NaCp$, in tetrahydrofuran (THF), yielded sublimable dark-red crystals of composition $U(C_5H_5)_3Cl$. Unlike the ionic cyclopentadienides of the lanthanide rare earth series, the actinide compound did not react in THF with $FeCl_2$ to form ferrocene. Other chemical and physical properties showed that covalent bonding rather than ionic bonding is important. For example, the absorption spectra of the lanthanide cyclopentadienides in THF show very sharp

bands reminiscent of those of the trivalent ion in aqueous solution. The absorption spectrum of UCp_3Cl showed no resemblance to the aqueous U^{IV} ion.

Trends for still heavier elements began to be established in 1965 when a group of workers at Karlsruhe prepared PuCp_3 , the first organometallic transuranium complex². The basic method of preparation devised by the German investigators has subsequently been applied to other transuranium elements up to element 98, californium. They reacted PuCl_3 with a melt of BeCp_2 on a vacuum-line to form PuCp_3 , which was found to be an extremely



Figure 1. Photomicrograph of californium tricyclopentadienyl single crystal

air sensitive pyrophoric compound sublimable at 140 to 165°C to form moss-green crystals. In 1966, the first organometallic compound of element 95, americium, was announced by the Karlsruhe group³. The compound, AmCp_3 , was made in a manner analogous to that used for PuCp_3 . The flesh-coloured sublimate was found to glow brightly from the alpha activity of the 434 year ^{241}Am .

In order to make weighable quantities of cyclopentadienyl compounds of the next three higher actinides, special micro-techniques had to be employed since only microgramme quantities of ^{249}Bk and ^{249}Cf were available at that time. The most plentiful isotope of curium, ^{244}Cm , is too radioactive (half-life of 17.8 years) to be very useful in organometallic chemistry. Preparations on the microgramme scale characterized the approach to chemistry in the transuranium area for many years, and the methods developed are still important. *Figure 1* is a photomicrograph of a single

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crystal of $^{249}\text{CfCp}_3$ weighing about one microgramme. It is shown in the 0.3 mm capillary in which it was prepared. This compound, synthesized by Laubereau and Burns in 1970, represents the current upper limit of atomic number for organometallic chemistry.

In order to make preparations of the type represented in *Figure 1*, special techniques were worked out, mainly by B. B. Cunningham and his students, over a period of years. Spectroscopic, magnetic, and other methods suitable for studies on the microgramme scale were also developed by Cunningham's group. The fundamental requirement in microgramme-scale chemistry is that impurities be rigorously excluded. Reagents must be of the highest purity and reaction vessels must be chosen carefully and pre-treated. A few microgrammes of an impurity leached out of a reaction vessel, for example, can completely nullify results obtained on a microgramme-scale preparation. Similarly, careful pre-purification of the actinide used in the preparation is required.

Air-dried bead diameter (μ)	Wet bead capacity (ng) (Act^{3+} , At. wt. = 250)
20	2.2
40	17.1
60	58
80	138
100	270
155	1000
195	2000

Figure 2. Dowex 50 \times 4 ion exchange resin capacity for trivalent actinides

The accurate analysis for impurities in microgramme quantities of the actinides is a difficult problem in itself. Although emission spectroscopic methods have been applied frequently in the past, they are inherently difficult and sometimes unreliable because of the many strong, often closely spaced lines of the transuranium elements. Mass spectrometric analytical methods are superior. A few microgrammes of ^{248}Cm used for preparing $^{248}\text{CmCp}_3$ were carefully purified at Oak Ridge. A mass spectrometric analysis carried out there gave the following impurities (in per cent): V, 0.05; Cr, 0.1; Fe, <1.0; Cu, 0.05; Zn, <0.5; Sn, 0.1; Zr, 0.1; Ba, <0.5; La, 0.02; Ce, 0.05; other rare earths, <0.02. It should be emphasized that these are, in some cases, upper limits dictated by the instrumental background. Impurities are more important in the heavy elements too because, for example, 1 per cent iron by weight is about 4 mole per cent in the curium.

Preparations on the microgramme scale can frequently begin conveniently by loading the actinide on a highly purified single ion exchange bead. This technique allows the maintenance of high purity during handling operations. Bead capacity is conveniently calibrated as a function of bead diameter. In *Figure 2* such a calibration is given.

The work of Laubereau and Burns^{4,5} is a good illustration of work on the microgramme scale. In their curium work, for example, seven microgrammes of ^{248}Cm were loaded onto a highly purified Dowex 50×4 ion exchange bead. A colourless bead of Cm_2O_3 was obtained by careful ignition at temperatures up to 1200°C . These ignitions were carried out by putting the bead in a platinum boat and heating the boat in an induction furnace.

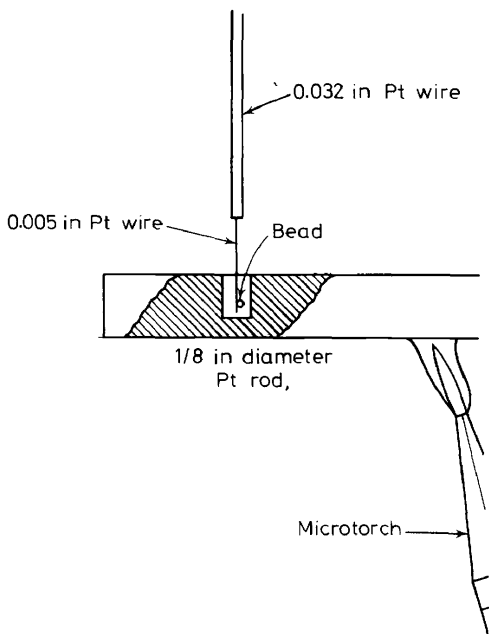


Figure 3. Calcination of actinide loaded micro resin bead

This step is illustrated in *Figure 3*, using a microtorch for the heating. Subsequently the bead was transferred to a capillary of about 0.3 mm diameter as shown in *Figure 4*. The oxide bead was picked up on a platinum wire that had been lightly coated with glycerine. It was then transferred to the capillary under the microscope and dislodged with a quartz fibre. The quartz capillary was attached to a reaction vacuum-line where it was evacuated to less than 10^{-6} torr. After heating to 530°C , highly purified HCl gas was introduced to start converting the bead to CmCl_3 . Three cycles of 530° , 560° , and 640°C were found to carry the reaction to completion. Volatile components were removed by keeping the bead under high vacuum for several minutes at 380°C . Melting of the CmCl_3 was not observed below 640°C although the reported melting point is 500°C . After these steps the chloride was reacted with BeCp_2 by subliming the latter into the quartz capillary from a side vessel. The reaction was carried out under normal pressure with purified argon as the inert gas. The reaction was allowed to proceed for 17 hours at a temperature of 70°C and then at 120°C for 30

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minutes. During this time the reaction mixture remained colourless. The colourless CmCp_3 was isolated in the upper part of the capillary by fractional sublimation as small crystals. A single crystal was subsequently grown and its space group and unit cell dimensions obtained by single crystal x-ray diffraction methods. These values compared to PrCp_3 were:

CmCp_3 , $a = 14.16 \text{ \AA}$, $b = 17.66 \text{ \AA}$, $c = 9.69 \text{ \AA}$, Pbcm

PrCp_3 , $a = 14.21 \text{ \AA}$, $b = 17.62 \text{ \AA}$, $c = 9.79 \text{ \AA}$, Pbcm

These data allow the calculation of a theoretical powder pattern to compare to the measured one and to the powder pattern of PrCp_3 . Of 19 lines allowed by theory, all 19 were found in the CmCp_3 powder pattern. These lines were found to agree closely in position and intensity with those of PrCp_3 , thus establishing the identity of the CmCp_3 compound.

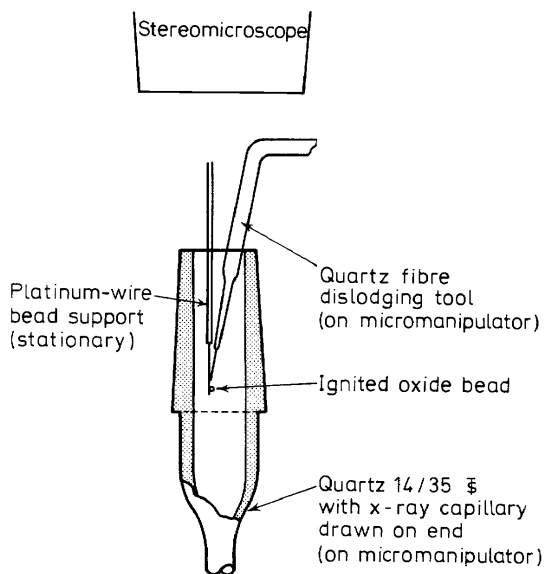


Figure 4. Transfer of actinide oxide bead to capillary

In spite of the difficulties, a group of workers centred at Karlsruhe⁶ obtained a mass spectrometric identification of CmCp_3 made with ^{244}Cm . This work, which was done independently and simultaneously with the work of Laubereau and Burns, also noted that a long-lived isotope was needed for preparative quantities to be produced.

One of the original interests in the cyclopentadienyls of the actinide elements stemmed from the need to see if their bonding would be significantly more covalent than the lanthanide elements. As already noted this is true in the case of UCp_3Cl . In contrast, the tricyclopentadienyls of plutonium through californium are regarded as being largely ionic in their bonding by the Karlsruhe^{2,3}, Oak Ridge^{4,7}, and Argonne⁸ groups that have studied them. For example, Nugent and associates⁷ deduced from the absorption

spectra of micro-crystals of CmCp_3 and Cm^{3+} in aqueous solution that the increase in covalency for the organometallic compound over the aqueous ion is relatively small. Similar conclusions were reached about AmCp_3 using data from Pappalardo and co-workers⁸. Thus, although the bonding in these actinide compounds is more covalent than in the analogous lanthanide compounds, they are still properly characterized as being highly ionic, and probably are more properly termed tricyclopentadienides than tricyclopentadienyls.

A new area of organometallic chemistry was opened in 1968 with the preparation of bis(cyclooctatetraenyl)-uranium(IV), $\text{U}(\text{COT})_2$, by Streitwieser and Müller-Westerhoff⁹. The new actinide compound was prepared by reacting uranium tetrachloride with potassium cyclooctatetraenide in tetrahydrofuran. The green plate-like crystals were found to be pyrophoric, but they were stable in water, acetic acid, and aqueous sodium hydroxide. $\text{U}(\text{COT})_2$ is also thermally stable and sublimes at 180°C at 0.03 mm. On the basis of its chemical properties $\text{U}(\text{COT})_2$ is clearly covalent since even the slightest dissociation would result in hydrolysis. Streitwieser and Müller-Westerhoff postulated in their original note that $\text{U}(\text{COT})_2$ was a sandwich π -complex analogous to ferrocene and they therefore proposed the name uranocene. Twenty-electron π -systems, such as offered by the two COT^{2-} rings, are allowed by symmetry to be shared in certain vacant f-orbitals on the uranium. In particular the $E_{2u} \rightarrow f_{xyz}, f_{z(x^2-y^2)}$ symmetry combination is allowed. Also two electrons furnished by U^{4+} can back bond in the symmetry allowed combination $E_{3u} \leftarrow f_{x(x^2-3y^2)}, f_{y(3x^2-y^2)}$. This interpretation, if correct, would mean that $\text{U}(\text{COT})_2$ is the first example of a π -sandwich complex with f-electrons involved in the bonding. Other evidence consistent with this interpretation was obtained in the single crystal x-ray diffraction study of Zalkin and Raymond¹⁰. In *Figure 5* the molecular symmetry is shown to be D_{8h} as required for the π -sandwich compound. The uranium-carbon bond lengths are all equal, having a value of $2.648 \pm 0.005 \text{ \AA}$. The individual rings were found to be planar within about 0.02 \AA . The equality of the bond lengths and the planarity of the ligands support the chemical evidence that $\text{U}(\text{COT})_2$ is properly named uranocene. This interpretation has recently been opened to question, however, by Edelstein, LaMar, Mares, and Streitwieser¹¹. Using proton magnetic resonance, these workers came to the conclusion that sigma bonding is important in $\text{U}(\text{COT})_2$ and perhaps dominates over π -bonding. Further investigations are required, however, to arrive at quantitative results and to treat the question of 5f-electron participation in the bonding*.

Work is also proceeding with heavier actinides. Karraker, Stone, Jones, and Edelstein¹² have carried out preliminary studies on $\text{Np}(\text{COT})_2$ and $\text{Pu}(\text{COT})_2$. Both were found to be stable towards water and dilute base. Mössbauer and absorption spectra and magnetic susceptibility measurements gave results differing considerably from ionic compounds. More detailed studies must be done, however, before a quantitative interpretation is possible.

Recently Mares, Hodgson, and Streitwieser¹³ prepared COT complexes of several lanthanide rare earths. These compounds were of the form

* Their recent work indicates predominantly π -bonding²¹.

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$\text{KLn}(\text{COT})_2$ where $\text{Ln} = \text{Ce, Pr, Nd, Tb, and Sm}$. They all react readily with water and alcohols. The cerium compound dissolved in tetrahydrofuran (THF) reacted immediately with UCl_4 to give $\text{U}(\text{COT})_2$. These chemical reactions suggest strongly that the bonding in the lanthanide compounds is ionic.

The study of the bonding in the COT complexes is just beginning. It will be most interesting to extend these complexes to the heavier actinides. It appears possible to prepare weighable quantities up to californium, at least.

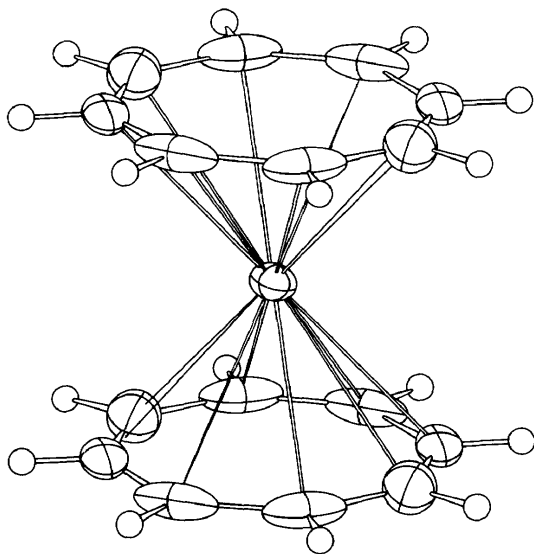


Figure 5. Molecular structure of $\text{U}(\text{COT})_2$. Reproduced by permission of American Chemical Society

The question is open at the present time about the organometallic chemistry of the highest atomic number elements since no appropriate experiments with these elements have yet been attempted. The elements toward the end of the actinide series and the beginning of the transactinide series are made one-atom-at-a-time on heavy ion accelerators such as the Berkeley HILAC (soon to be Super-HILAC), the Dubna U-300 (soon to be U-400), and the ORIC at Oak Ridge. The one-atom-at-a-time chemistry carried out at these three laboratories is suggestive as to how organometallic chemistry can be accomplished in this heavy region. The methods currently being worked out will also be required for chemical studies of the superheavy elements if they can be produced using the new accelerators.

The first consideration in planning chemical experiments in the heaviest elements is their half-lives. For example, the isotope of element 102 (nobelium) of mass 255 was used to establish its valence state in aqueous solution as +2. This isotope has a half-life of only 3 minutes. It is instructive to consider this classic work which was carried out by Silva and associates¹⁴. A few $^{255}_{102}$ atoms were produced per experiment by bombarding a target containing 74 per cent ^{244}Pu with ^{16}O ions. A gas jet system of the general type shown

in *Figure 6* was employed. The beam of ^{16}O ions comes in from the accelerator and is degraded to the proper energy for the reaction (97 MeV in this case) before it strikes the target. The plutonium target material was supported by a thin beryllium foil. The momentum of the impinging oxygen ions causes the 102 atoms produced to recoil into a stream of helium gas. The stream of gas sweeps these product atoms through a nozzle to a collector. In the drawing the set-up is for certain types of nuclear experiments. For the chemical experiments a rabbit system is substituted so that the gas jet blowing out of the nozzle deposits the 102 atoms on a rabbit. The rabbit is then blown out of the laboratory where the 102 atoms are washed off for the ion exchange study of 102 chemistry.

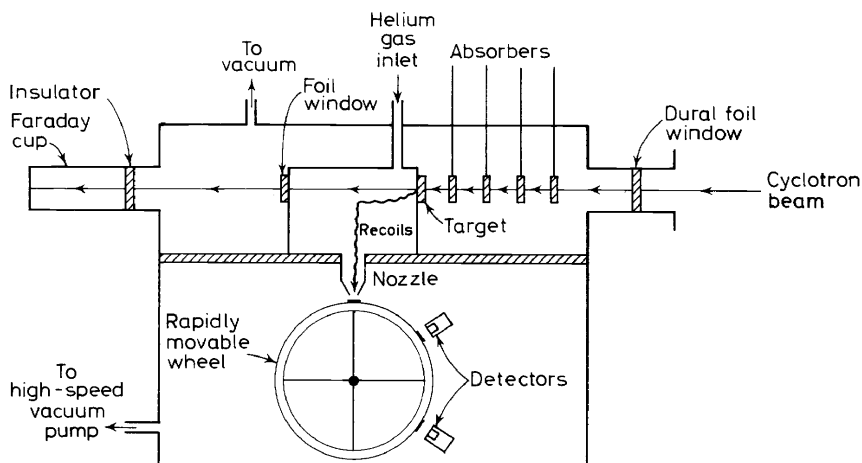


Figure 6. Schematic of gas jet system (top view)

In *Figure 7* the elution pattern is shown for element 102 in relation to the other actinides and the alkaline earths using ammonium α -hydroxyisobutyrate as the elutriant on a heated Dowex 50×12 cation exchange column. Trivalent element 102 would elute in the pre-einsteinium position on the far left of the figure, but the actual position is found to be on the right side of the actinides toward the divalent alkaline earths. Thus, under normal aqueous conditions, element 102 does not show a resemblance to the trivalent actinides, but rather shows that it is stable in the divalent state in aqueous solution. This finding was a confirmation of Seaborg's prediction 20 years before this experiment was performed of a possible stable +2 state for element 102 due to the special stability of the $5f^{14}$ -electronic configuration.

Elements 104 and 105 have still shorter half-lives than element 102. The longest-lived isotope of element 104 is the isotope of mass 261 with a half-life of about one minute¹⁵. An isotope of 105 has been reported with a half-life of 40 seconds¹⁶.

It is important, of course, to discover isotopes of these heavy elements with half-lives as long as possible in order to open up the broadest range of

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studies of their chemistry. Work is currently under way that indicates that a new isotope of element 102 of mass 259 has been synthesized which appears to have a half-life of about an hour¹⁷. Similar studies indicate that a new isotope of element 103 with a half-life of perhaps 3 minutes can be made¹⁸. These new isotopes, if their existence is confirmed, will make it possible to do more intricate experiments than have previously been possible for these two elements.

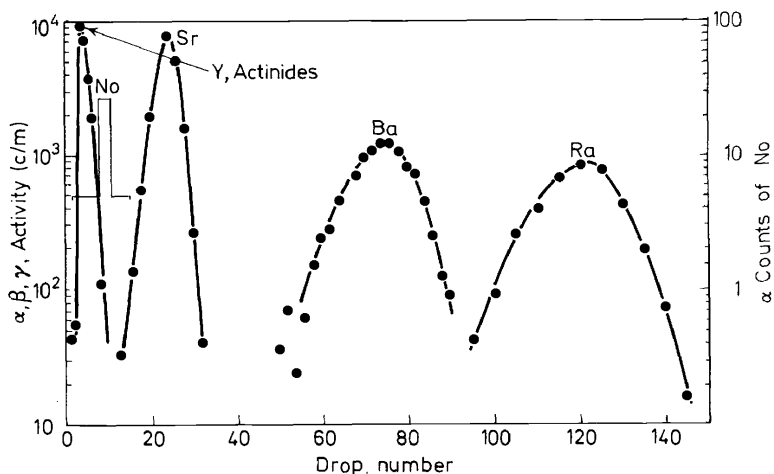


Figure 7. Ion exchange elution position of nobelium (No) relative to the other actinides and to the alkaline earths. Reproduced by permission of American Association for the Advancement of Science

For isotopes with very short half-lives, gas chromatographic methods are used. A system developed by Zvara and Zvarova¹⁹ (Figure 8) appears promising for the study of accelerator-produced isotopes. Aluminium chloride vapour, Al_2Cl_6 , is reacted with a lanthanide or actinide chloride in the heat boat (11). The volatile compound or compounds formed are carried by a flowing gas stream through the spiral chromatographic column in the furnace (1). Fractions of the condensate are collected by pulling out the

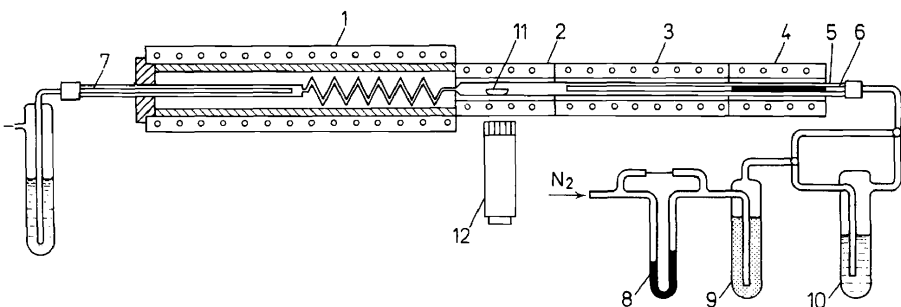


Figure 8. Gas chromatography system

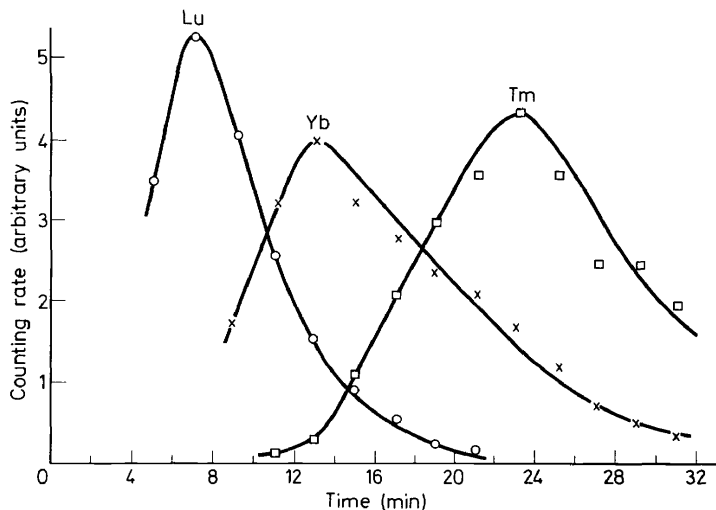


Figure 9. Thulium-ytterbium-lutetium separation

tube (7) one centimetre every two minutes. For β - and γ -emitting isotopes, the elemental separation can be detected directly along the tube. For α -emitters, a fraction from each section of the tube was dissolved in HCl and a source made for counting from the solution. In Figure 9 some results on the heaviest lanthanides are shown. Since the heaviest lanthanides and actinides are the most difficult to separate, these results for Lu, Yb, and Tm are impressive. Zvara and Zvarova have also obtained interesting results in the actinide series²⁰ as shown in Figure 10 where americium, curium, and plutonium are shown to be nicely separated.

The techniques being pioneered by Silva and co-workers and by Zvara and co-workers are paving the way for the study of organometallic chemistry in this heaviest element region. Thus the understanding of the metal-carbon

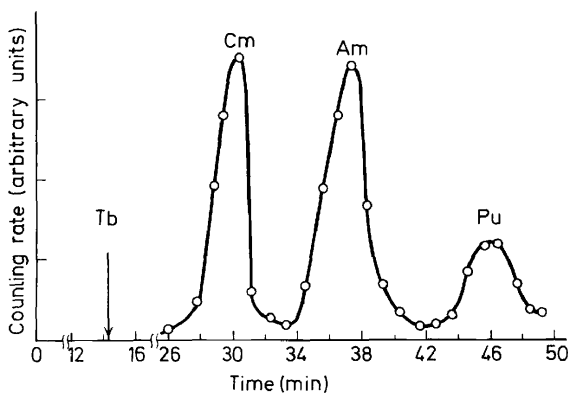


Figure 10. Curium-americium-plutonium separation

bond at the end of the actinide series and the beginning of the transactinide series poses an important challenge for organometallic chemistry in the future.

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