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# Chemical Analysis of Organometallic Compounds

Volume 5. Elements of groups VIA, VIB, VIIA, VIIB,  
aluminium and zinc

T. R. CROMPTON

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*Goosnargh, nr. Preston,  
Lancashire*

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# **Chemical Analysis of Organometallic Compounds**

# THE ANALYSIS OF ORGANIC MATERIALS

An International Series of Monographs

edited by R. BELCHER and D. M. W. ANDERSON

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## PREFACE

It occurred to the writer following the interest shown in his earlier book on the "Analysis of Organoaluminium and Organozinc Compounds" that it would be a worthwhile project to write a more comprehensive work which dealt with the analytical chemistry of the organometallic compounds of all the elements in the periodic table. The writer was delighted, therefore, to be approached by the editors of this series with a proposal to write such a book.

Chapters have been arranged on the basis of the group classification of the periodic table. This volume covers Groups 6 and 7 of the periodic table. Also included in this volume is a Chapter dealing with the organometallic compounds of aluminium and zinc. This was not included in its logical place in Volume 1 of this series because the author had previously written a book covering these elements ("Analysis of Organoaluminium and Organozinc Compounds" (International series of Monographs in Analytical Chemistry, Volume 31, Pergamon Press, 1968)). This latter book is now out of print.

The arrangement of material within each Chapter is based on the most logical sequence possible bearing in mind the wide variety of techniques that have been used and the variety and complexity of types of organometallic compounds of some of the elements discussed. Each Chapter starts with a discussion of the determination of elements and of functional groups. Following this there are various other sections comprising different techniques for analysis of different classes of compounds of the element concerned. With most elements gas chromatography has been applied and this important technique is discussed in detail in a separate Section, as are the various spectroscopic techniques.

Throughout the volumes, particular emphasis will be placed on the inclusion of detailed analytical procedures to enable the reader to apply the method without further reference to the original source. Reference to a particular instrument manufacturer in these methods merely implies that their instrument was available to the original workers. No doubt, comparable models of other manufacturers could be used provided they meet the specification indicated in the method.

It is hoped that the books will interest workers in a wide variety of fields both industrial and Academic, and both the pure and applied ends of the subject. Organometallic chemistry is a growing field to which students should direct their interest, and it is hoped that they will find much to interest them.

*"Beechcroft",  
Whittingham Lane,  
Goosnargh, nr Preston,  
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January 1977*

*T. R. Crompton*

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## **16. GROUP 6A ELEMENTS: ORGANOCOMPOUNDS OF CHROMIUM, MOLYBDENUM, TUNGSTEN AND URANIUM**

Very little information has been found concerning the analytical chemistry of the organometallic compounds of chromium, and no references have been found to organometallic compounds of tungsten. The only references of any relevance found in the case of molybdenum and uranium concern the carbides of these elements.

### **I. ORGANOCHROMIUM COMPOUNDS**

#### **A. Determination of Chromium**

Kalinovskaya and Silvestova (1968) have described a procedure for the determination of chromium in organochromium complexes used as additives in drilling fluids. The sample solution (50 ml containing less than 5 mg of dry residue and less than 52  $\mu\text{g}$  of chromium) is evaporated to dryness on a water bath, and the residue is mixed with 1 ml each of conc nitric acid and 5% potassium chlorate solution, and again evaporated to dryness; if this residue is green or dirty, a lesser weight of sample is used. The residue is dissolved in water and the solution is boiled with 2 ml of 2.5 M sulphuric acid and 2 drops of 2.5% silver nitrate solution, then gently boiled for 30 min with 0.1 g of ammonium persulphate, 0.4 ml of 5% sodium chloride solution is then added, the mixture is filtered, and chromium in the filtrate is determined with diphenylcarbazide.

#### **B. Mass Spectrometry**

Booker and Isenhour (1969) have described a rapid mass spectrometric determination of chromium as chromium(III)hexafluoroacetylacetonate. The determination can either be directly applied to nanogram samples or to larger

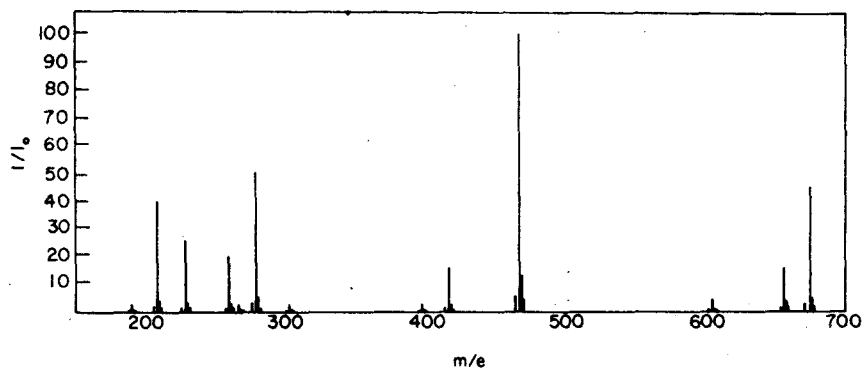


FIG. 208. Mass spectrum of chromium hexafluoroacetylacetonate ( $\text{Cr(hfa)}_3$ ) above mass 200.

samples such as stainless steels containing several percent chromium by aliquoting. In this procedure about 25 mg of the chromium-containing sample is quantitatively oxidized with perchloric acid in a sealed tube and then reacted with hexafluoroacetylacetone to produce chromium(III) hexafluoroacetylacetonate. This chelate is then quantitatively transferred as an ether or benzene solution to the inlet block of an MS9 mass spectrometer. Figure 208 shows a mass spectrum of the compound above mass 200; the relative intensities and mass assignments for the major peaks are given in Table 221.

Table 221. Relative intensities and mass assignments for the mass spectrum of chromium hexafluoroacetylacetonate.

<i>m/e</i>		PFTBA Peak	Ratio	<i>I/I</i> <sub>0</sub>	Fragment
Calcd	Found				
672-9046	672-8906	613-9647	1.095976	45	$\text{Cr(hfa)}_3^+$
653-9062	653-8982	613-9647	1.065042	10	$\text{Cr(hfa)}_3\text{-F}^+$
603-9094	603-8868	501-9711	1.203031	5	$\text{Cr(hfa)}_3\text{-CF}_3^+$
465-9169	465-9685	463-9743	1.004298	100	$\text{Cr(hfa)}_2^+$
415-9188	415-9187	413-9775	1.004689	15	$\text{Cr(hfa)}_2\text{F-CF}_3^+$
396-9214	396-9157	375-9807	1.055681	<5	$\text{Cr(hfa)}_2\text{-CF}_3^+$
—	301-9537	263-9871	1.143820	<5	—
277-9269	277-9238	263-9871	1.052793	50	$\text{Cr(hfa)F}^+$
—	267-4465	218-9856	1.221297	5	—
258-9285	258-9218	218-9856	1.182369	20	$\text{Cr(hfa)}^+$
227-9301	227-9281	218-9856	1.040836	25	$\text{Cr(hfa)F}_2\text{-CF}_3^+$
208-9317	208-9252	180-9888	1.154354	40	$\text{Cr(hfa)F-CF}_3^+$
189-9333	189-9259	180-9888	1.049379	5	$\text{Cr(hfa)-CF}_3^+$

This spectrum is characteristic of chromium hexafluoroacetylacetonate for ionizing voltages greater than 25 V. The most prominent peak is that assigned to,  $^{52}\text{Cr}(\text{hfa})_2$  ( $I/I_0 = 100$ ), and this peak is used. A calibration curve is shown in Fig. 209.

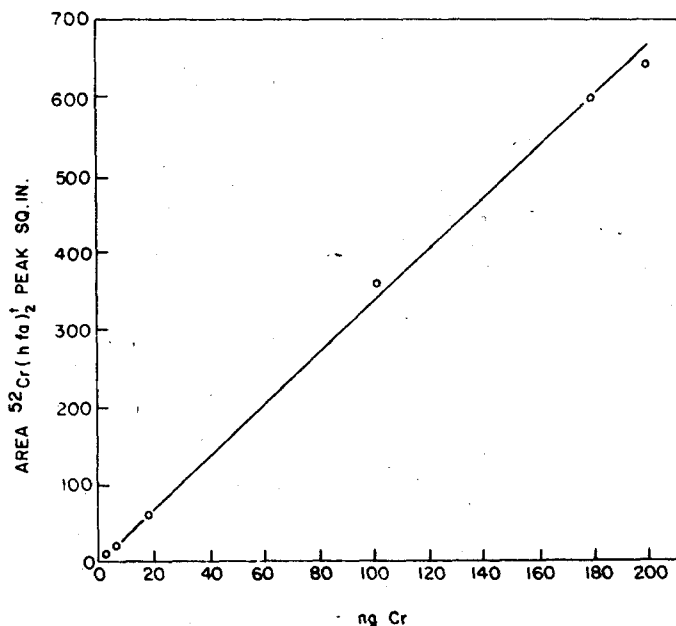


FIG. 209. Integrated area of  $^{52}\text{Cr}(\text{hfa})_3$  Peak vs. weight of chromium (hfa = hexafluoroacetylacetonate).

### C. Determination of Chromium Soaps

Malik and Ahmed (1964) have devised rapid spectrophotometric methods for the estimation of chromium stearate used as additives in lubricating oils. They found that when chromium stearate is heated with *o*- or *m*-toluidine at  $180^\circ$  to  $200^\circ\text{C}$  for about 20 min, complexes are formed having maximum extinctions at 480 and 540 nm respectively. Beer's law is obeyed for concentrations of 1.2 to 10.7 mg per ml, so that the metal ion content of the soap can be determined even in dilute solution. These workers (1965a, 1963) also studied the spectrophotometric behaviour at 425 nm of chromium(III) and stearates, in amounts between 1 and 14 mmole  $\text{l}^{-1}$ , in non-aqueous solution. Malik and Ahmed (1965b) determined the viscosity of non-aqueous solutions of chro-

mium soaps and used this as a basis for estimating these substances in the range 1 to 27 g l<sup>-1</sup>.

## II. MOLYBDENUM, TUNGSTEN AND URANIUM CARBIDES

Nazarchuk and Pechentrovskaya (1961) and Popova and Zaslavskaya (1956) have described colorimetric procedures for the determination of free carbon in molybdenum and tungsten carbides.

Atoda *et al.* (1961) have described procedures for the estimation of quadrivalent and hexavalent uranium and free and total carbon in uranium carbides. Quadrivalent uranium is determined by adding 6N sulphuric acid (20 ml) and a known volume of 0.03N ceric ammonium sulphate ( $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ) to the sample (0.05 g) and heating for 1 h to dissolve the oxide. The yellow solution is cooled to 20°C, 0.001M 1,10-phenanthroline (0.3 ml) is added, and the excess of quadrivalent cerium titrated with 0.03N ferrous ammonium sulphate. Towards the end of the titration conc phosphoric acid (2 ml) is added to ensure that the colour of the indicator changes from pale blue to pink at the end-point. The hexavalent uranium concentration is determined by subtracting the weight of quadrivalent uranium from the total weight of uranium in the sample. Total uranium is determined by igniting the sample (0.3 g) at 900° for 1 h, treating the resulting oxide with 3N nitric acid (30 ml) and evaporating to dryness. To the warm residue is added 6 N sulphuric acid (10 ml) and after the evolution of white fumes for 10 min, the solution is cooled, 6 N sulphuric acid (10 ml) added, and the solution again heated to fumes. The solution is cooled and diluted to 100 ml with water and an aliquot (25 ml) is mixed with 6 N sulphuric acid (20 ml) and passed at 15 ml per min through a Jones reductor filled with zinc amalgam. After the reductor has been washed out, air is bubbled through the solution and washings for 5 min to oxidise any trivalent uranium, then 0.001 M 1,10 phenanthroline is added, and the solution titrated with 0.03 N ceric ammonium sulphate ( $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ). Total carbon is determined by burning the sample (0.2 to 0.4 g) in a current of oxygen and collecting the carbon dioxide. Free carbon is determined by heating the sample (0.5 to 1 g) with 3 N nitric acid (30 ml) on a water bath for 3 h. The insoluble residue of free carbon is collected on a filter of ignited asbestos and washed with 2 N sodium hydroxide, then with N hydrochloric and hot water. After the residue has been dried at 110°C, the asbestos and free carbon are burned in a combustion tube and the quantity of carbon dioxide produced measured. Atoda *et al.* (1961) found that this method had coefficients of variation of 0.1 % (total uranium), 0.05 % (total carbon) and 0.02 % (free carbon).

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## 17. GROUP 6B ELEMENTS: SELENIUM AND TELLURIUM

Sulphur is not discussed in these volumes. No reference in the analytical literature has been found to organocompounds of polonium.

### I. ORGANOSELENIUM COMPOUNDS

#### A. Determination of Elements

##### *Selenium*

Various techniques have been employed for the determination of selenium in organoselenium compounds. These include combustion techniques, oxygen flask combustion, fusion with sodium peroxide and digestion with acids.

Zabrodina and Bagreeva (1958) described a method for the microdetermination of selenium in organic compounds containing carbon, hydrogen, oxygen and nitrogen. This method involves tube combustion of the sample in oxygen. The ignition tube consists of a 50 cm tube of diameter 9 to 10 mm, narrowing at the exit-end to 3 mm; the narrow tube is bent through a right angle and dips into 7 or 8 ml of water in a 10 ml cylinder. An electric furnace set at 800° to 900°C is placed 6 or 7 cm from the constriction, and the sample (4 to 6 mg, 0.8 to 3 mg of selenium) is placed 3 or 4 cm from the furnace. The sample is ignited with a burner in a stream of oxygen flowing at a rate of 20 to 25 ml per min; white crystals of selenium dioxide form on the walls of the tube beyond the furnace—this section of the tube is preferably cooled with wet cotton wool. After the ignition the furnace is removed and the tube clamped at an angle and the sample left to cool in the flow of oxygen. The oxygen intake is replaced with a Mariotte flask serving as an aspirator, the tap is opened and the water sucked up to just beyond the layer of sublimed selenium dioxide. The tap is closed and the Mariotte flask removed to allow the solution of selenous acid to drain into the cylinder from which it is poured into the titration flask. The rinsing is repeated twice, carefully heating the tube when the final rinse is carried out. The selenous acid solution is evaporated