

**THE INORGANIC ANALYSIS  
OF PETROLEUM**



# THE INORGANIC ANALYSIS OF PETROLEUM

by

**JAMES W. McCOY**

*Supervising Chemist, Analytical Laboratory  
Standard Oil Company of California  
Western Operations, Inc.  
Richmond, California*



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## PREFACE

Although many papers have been published describing methods for the inorganic analysis of petroleum no book has previously appeared devoted exclusively to this subject. The purpose of this work is to provide a laboratory handbook for industrial analysts of various degrees of professional training covering the determination of those elements commonly occurring in various types of petroleum products. The procedures represent, from the author's point of view, a reasonable compromise among the usual conflicting interests of speed, accuracy, and cost, and emphasize manufacturing rather than research applications.

The usual industrial method is written to apply to specific products wherein the element to be determined is normally present within rather well-defined limits of concentration. These methods are then followed as recipes with more or less satisfactory results. Products for which this type of method is prescribed can often be handled very well by instrumental methods of analysis. In spite of the numerous papers on instrumental analysis, however, and the large volume of advertising of this trend, wet chemical methods still predominate in the daily work of a refinery laboratory, and will no doubt continue to do so.

The methods in this book are written to apply to as great a variety of products as possible. Throughout the book, however, suggestions are made which should enable the user to modify or shorten the procedures for specific purposes. Numerous notes have been included in the procedures, which the author believes will be helpful; the information they contain is more easily expressed in this way than by extensive discussion sections.

A separate chapter is devoted to each element, and the chapters are arranged in alphabetical sequence by element except bromine, chlorine, and fluorine which are covered in one chapter under the generic name halogens.

It is appropriate to acknowledge here the generous assistance of a number of persons during the years while this book has been in preparation. I know no more able chemist than Mr. Leo Heller of the California Chemical Company, and to him I express special appreciation for many helpful and instructive discussions during twelve years of association. Without the interest and encouragement of Mr. R. C. Vollmar, Chief Chemist of the Richmond Refinery, this book could not have been produced, and it is a pleasure to acknowledge his cooperation in making its publication possible. The evaluation of the analytical procedures was materially aided by the careful work of a number of my associates in the analytical laboratory at Richmond, notably: Messrs. J. A. Bertera, E. I. Pollard, M. G. Smith, D. L. Spurlock, and W. T. Werner.

Finally, I am indebted to my wife for her assistance with the reading of proof; to Mrs. Nora Hutton, for much of the preliminary stenographic work; and, with special thanks, to Mrs. Rosemarie M. Wildebaur, who so ably and so cheerfully accomplished the tedious task of typing the manuscript.

JAMES W. McCOY

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**THE INORGANIC ANALYSIS  
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# INTRODUCTION

In the following chapters, methods for determining twenty-four common chemical elements naturally present in or purposely added to petroleum and its products are described in detail. It is presumed that, in general, a petroleum analytical laboratory is concerned with non-routine analyses, and with procedures that are hazardous, or require special equipment; for the most part, the book is concerned with these types of analyses, with emphasis on wet chemical methods.

The methods of the American Society for Testing Materials, issued annually by the D-2 Committee on Petroleum Products and Lubricants, have been standard in the petroleum industry for many years, and the methods given in this book are meant to supplement rather than supplant the ASTM Standards. Widely used ASTM procedures, such as the determinations of tetraethyllead by acid extraction, and of sulfur by lamp, or methods with oxygen bomb, are not considered here, for it can safely be assumed that analysts in the petroleum industry are familiar with these methods and already use them regularly.

In Chapter 1, a short account is given of the usual natural inorganic components of petroleum and a number of additives are briefly described. The inorganic analysis of petroleum does not differ materially from that of any other substance once the solution to be analyzed has been prepared. The choice of the method for decomposing the petroleum sample is of paramount importance, however, and this subject is considered in detail in Chapter 2. In subsequent chapters, methods are given for determining the individual ele-

ments in various types of samples. In developing these methods for particular applications, frequent use has been made of standard works on inorganic analysis, especially: *Applied Inorganic Analysis* by Hillebrand, Lundell, Hoffman, and Bright; and Sandell's *Colorimetric Determination of Traces of Metals*.

It is assumed that common laboratory instruments, including electrolytic equipment, pH meters and potentiometers, and spectrophotometers, are available. Less common equipment, such as flame photometers, polarographs, emission spectrographs, and X-ray fluorescent spectrometers, are omitted here, or mentioned but briefly.

The important problem of sampling petroleum is the subject of an ASTM publication, *ASTM Manual on Measurement and Sampling of Petroleum and Petroleum Products*. The usual difficulties of mixing, dirty containers, contaminated sample lines, and possible effects of the material of the sample on the container are always a consideration, and for all these specific recommendations are made in the individual chapters.

## Chapter 1

# THE INORGANIC COMPONENTS OF PETROLEUM

Much effort has been directed to ascertaining the origin and the conditions of formation of petroleum accumulations. A knowledge of the geological relationships, the depths and ages of pools, and their compositional characteristics is useful in exploring and judging the prospects of undeveloped areas. Several hypotheses have been advanced to account for the evolution of petroleum from deposits of organic material in marine sediments into the final form in which it is found today.<sup>1</sup>

The organic origin of petroleum is indicated by the presence of chlorophyll derivatives, nitrogenous compounds, and optically active substances.<sup>2</sup> Marine sediments contain great quantities of micro-organisms, and their role in the formation of petroleum has been investigated.<sup>3</sup> Bacterial reduction usually stops at the production of carboxyl, hydroxyl, amino, and sulfhydryl groups rather than continuing in complete reduction to hydrocarbon, although methane-producing anaerobic bacteria are common. The most likely sources of petroleum are the fatty oils, however, and these are very resistant to bacterial action.

The development of a general theory for the mechanism of petroleum evolution is hampered by the absence of any deposits of intermediate age. There is, however, considerable evidence of catalytic polymerization at low temperatures, and cracking by acid silicates, clays, and sedimentary silicate rocks. A comprehensive review of this evidence has been made by Brooks.<sup>4</sup> The presence of porphyrins and other

heat-sensitive substances in petroleum indicates that extreme temperatures did not prevail during the history of formation; the upper limit may have been 140°F, and there is no evidence that high pressures were a factor in the cracking process.

Crude oils produced from very old sedimentary rocks tend to be light paraffinic products containing a large proportion of hydrocarbons of low molecular weight, low in nitrogen and oxygen. Younger formations are heavy naphthenic oils with very little of light hydrocarbons, and appreciable amounts of nitrogen and oxygen. As asphalt appears to be a primary substance, it is likely that asphaltic crudes were laid down in reservoir rocks without catalytic properties.

Many different metallic elements have been reported in crude petroleum. In a study of the oil-soluble components of 25 different crude samples, Jones and Hardy<sup>5</sup> found the most prevalent to be aluminum, calcium, iron, nickel, silicon, sodium, and vanadium. Of these, sodium and vanadium ordinarily comprise more than ten per cent of the total ash; in only a few instances was vanadium less than one per cent. A number of the crudes contained chromium, copper, lead, magnesium, and manganese to the extent of one-tenth to one per cent of the ash, and isolated samples contained traces of boron, cobalt, molybdenum, platinum, potassium, silver, strontium, and titanium. The oil-soluble forms include porphyrin-metal chelated complexes, and probably other complexes with nitrogen-containing compounds and soaps. As these are effective emulsifying agents, they hold water or brine in extremely stable emulsions. Dodd *et al.*<sup>6</sup> have investigated the film-forming characteristics of crude oils containing metallic complexes. Metals may occur in the same crude in more than one form; and inorganic forms may be present in highly dispersed suspensions, or in the colloidal state.<sup>7</sup>

The properties and structures of the porphyrin complexes have been studied rather extensively,<sup>8,9</sup> and Groennings<sup>10</sup> has developed a quantitative method for the determination of porphyrins in petroleum. Beach and Shewmaker,<sup>11</sup> as a result of extraction studies, have established two classes of vanadium compounds in petroleum. Class I comprises those that are extractable with aqueous pyridine; and Class II



comprises those that are not extractable. By conducting molecular distillations with castor oil as a carrier they estimated the equivalent atmospheric boiling points of the volatile porphyrins to be in the range of 1085° to 1200°F, with molecular weights in the 543–800 range. From measurements of absorbency they conclude that the difference in the volatile and non-volatile aggregates is probably in the peripheral groups rather than in the nitrogen-vanadium bonds; and that the non-volatile porphyrins have large asphaltic or polymeric side chains which distort the nitrogen-vanadium bonds and produce a non-characteristic spectrum. The vanadium porphyrins have been most thoroughly investigated. Nickel porphyrins have similar properties, and it will be seen later that their respective volatilities are important considerations when determining the concentrations of these elements by chemical methods.

Table 1 shows the analyses of six different random samples of crude oils. These are given to show the rather wide range in concentrations of the common elements, but they are not necessarily typical of the particular crudes. The California sample is from the Midway field, and is of interest as the youngest petroleum formation in the United

TABLE 1:1  
ANALYSES OF CRUDE OILS

<i>Element</i>	<i>Source</i>					
	ARABIA	CALIFORNIA	CANADA	COLORADO	SUMATRA	VENEZUELA
	parts per million					
Al	0.40	1.3	0.50	0.50	0.80	0.40
Ca *	3.0	7.0	—	—	5.0	10.00
Cr	0.160	—†	0.040	0.080	—	1.10
Cu	0.330	0.80	0.160	0.320	0.20	1.80
Fe	1.20	18.0	2.20	1.30	1.60	14.0
Ni	5.30	31.0	1.60	0.40	8.0	112.0
Si	7.40	3.0	6.90	5.60	—	10.0
Na	0.70	3.90	13.0	4.10	3.90	28.0
V	13.0	7.0	0.84	1.9	0.18	1290.0
	percent					
Ash	0.004	0.009	0.009	0.009	0.004	0.21
N	0.095	0.420	0.098	0.098	0.110	0.65
S	2.10	0.660	0.740	0.740	0.110	5.50

\* Determined spectrographically.

† Dashes indicate element not determined.

States. It is estimated to be between ten and thirteen million years old.<sup>4</sup>

In addition to the metallic elements originally present in crude oil, several others are often introduced in removing it from the ground. Emulsified brine and drilling muds (bentonites weighted with barite or hematite) account for the presence of such salts as aluminum, barium, calcium, iron, magnesium, and sodium, combined with bicarbonate, chloride, silicate, and sulfate. These salts are extractable with hot water if a demulsifier is added. The presence of chlorides is especially objectionable because the hydrolysis of these salts produces hydrochloric acid, which causes extensive and rapid corrosion. The pyrolytic decomposition starts at the rather low temperature of 250°F; this type of corrosion introduces additional metals from condensers and piping. A further source of contamination during refining is from the attrition of various catalysts. Crudes containing aliphatic and naphthenic acids are also very corrosive, and they introduce oil-soluble contaminants into petroleum unless they are neutralized early in the refining. Sour crudes containing hydrogen sulfide and mercaptans are destructive to equipment and require special handling.

Although the total ash of crude oil seldom exceeds .05 per cent, and is often as little as 0.001 per cent, the processing of large amounts of petroleum leads to the rapid accumulation of large concentrations of ash in the residua, and consequent mechanical plugging of furnace tubes and related equipment, unless the oil is desalted beforehand. As mentioned before, the volatility of certain metallic compounds may lead to their presence in distillate fractions, their concentrations increasing with the depth of the cut. Some of these alter the selectivity of cracking catalysts,<sup>12</sup> increasing the formation of coke and hydrogen and decreasing the yield of gasoline. The more common metals of this type are nickel, copper, vanadium, and iron. Others, in particular the alkali metals, decrease catalytic activity by participating in what is commonly called an acid-base reaction with the acidic catalyst (probably more properly classified as ion-exchange). This latter effect is permanent and the alkali and alkaline earth metals are true poisons.

Non-volatile vanadium, which concentrates in the re-

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