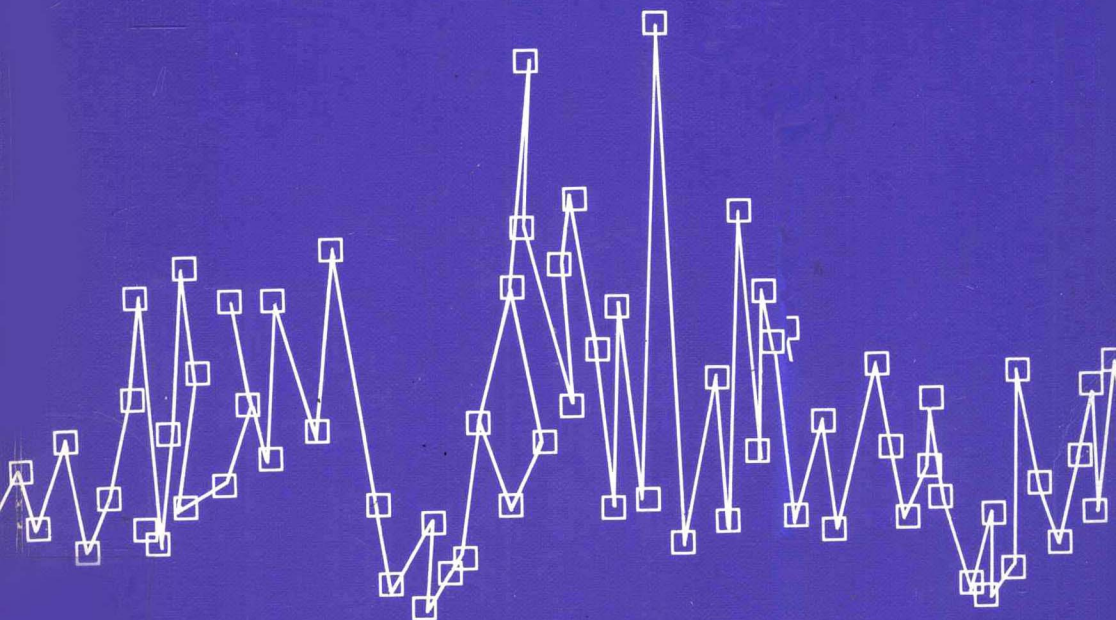# Modern Instrumental Methods of Elemental Analysis of
PETROLEUM PRODUCTS AND LUBRICANTS

R. A. Nadkarni, editor

ASTM

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Modern Instrumental Methods of Elemental Analysis of Petroleum Products and Lubricants

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to time and effort on behalf of ASTM.

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Overview

The last two decades have seen explosive growth in the development and use of analytical instrumentation in all areas of science. The field of petroleum and fuel science has certainly been no exception to this trend. In a commercial or industrial laboratory nowadays, one will rarely find classical wet chemistry techniques being used for elemental analysis. These are being increasingly replaced by modern instrumental techniques such as atomic absorption (AA) spectrometry, inductively coupled plasma atomic emission spectrometry and mass spectrometry, X-ray fluorescence (XRF), ion chromatography, and so on. Even a reasonably modern and universally used technique such as atomic absorption spectrometry is widely being replaced by a newer and better technique, inductively coupled plasma atomic emission spectrometry (ICPAES).

In spite of the advances in analytical technology, many product specifications continue to be written with older test methods specified for analysis, even though very few, if any, laboratories may be using these methods (e.g., ASTM D 811). Hence a symposium was organized by ASTM Committee D-2 on Petroleum Products and Lubricants and its Subcommittee D02.03 on Elemental Analysis to provide analysts and marketers with information on state-of-the-art methodology for the elemental analysis of petroleum products and lubricants. The symposium was held in New Orleans, Louisiana, on 11–13 December 1989 and was attended by over 150 people from nine countries. Twenty papers were presented at the symposium, from which thirteen are included in this ASTM Special Technical Publication. The papers have been arranged by analytical techniques, although some papers fall into more than one category.

The first two papers are comprehensive reviews by *Nadkarni*, the first describing the occurrence and significance of trace metals, the second presenting current analytical technology for elemental determination in petroleum-related materials. Trace metals in crude oils originate from the marine animal and vegetative source of crude oils. Many metals are present as porphyrin complexes and are often used as the biomarkers for the origin of crude oil. On the other hand, several metals may be added during refining to the petroleum or to the lubricating oils for diverse beneficial physical performance. Part I discusses comprehensively the role of various metals added to lubricants, the significance of trace elements found in used lubricating oils, and the various standard reference materials that can be used for quality assurance of petroleum analysis. ASTM publishes nearly 45 methods for the elemental analysis of petroleum products. Part II covers the diverse sample preparation schemes necessary for certain analytical techniques, and then reviews the principles and applications of each of the major techniques. The review covers atomic absorption spectrometry with and without flame, inductively coupled plasma atomic emission spectrometry, microelemental methods, neutron activation analysis, spark source mass spectrometry, X-ray fluorescence, and ion chromatography. Most of these techniques are fully matured and have been extensively documented in the literature. Yet no one technique can be ideal for all types of analyses. An analyst must make a pragmatic choice based on specific criteria for a specific matrix for a particular analysis.

Mackey et al. compare ICPAES and XRF as two alternative techniques for the determination of additive elements in lube oils, as practiced in their laboratory. The aim of the paper is to help the nonexpert get a better understanding of the advantages and drawbacks of these two techniques.

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The next five papers deal with atomic spectroscopy analysis, both for crude and used oils and additives. *Gonzales and Lynch* describe an ICPAES method for the determination of 18 trace elements in crude oil. Optimum conditions for solvent selection, proper wavelength, and use of internal standard result in recoveries greater than 90% for the elements of interest.

Carter et al. describe an automated rapid multielement determination of wear metals in used oils using flame AA with a single aspiration per sample. This spectrometer can sequentially determine up to 24 elements per sample in a single run. The method appears much more powerful and streamlined than those using conventional AA instruments.

Lukas and Anderson describe three techniques that can be used to improve the ability of optical emission spectrometry to detect and quantify large wear particles in lubricating oil. These are the single spark, ashing rotrode, and acid digestion differential techniques. The technique of choice varies with the requirements and philosophy of the analytical laboratory.

In a similar comparison, *Nygaard et al.* compared 50 used and 20 new diesel engine oils for ten wear metals and four additive elements analyzed by ICPAES and rotating disk electrode spark emission spectrometry. Interestingly, the two groups of elements were found to respond differently to the two techniques. They were also affected by the sample viscosity. It is believed that rotrode is somewhat more effective in sampling particulates than is ICPAES.

The above papers attest to the continuing interest in the determination of wear metals in used oils using AAS or ICPAES. Currently, ASTM D02.03 is involved in completing an ICPAES test method for wear metals in used oils. A round-robin has been completed and the method is being ballotted.

The newly developed technique of inductively coupled plasma–mass spectrometry (ICP-MS) is the subject of a paper by *Williams*. She demonstrates the application of this technique to the determination of several environmentally important trace elements in recycled oils. The ICP-MS technique, even though widely used in geological and isotopic studies, lags far behind ICPAES in terms of its use in the petrochemicals industry. The cost and complexity of the instrument as well as the wide use of ICPAES have contributed to this situation.

A technique as important as atomic spectroscopy in petrochemicals analysis is X-ray fluorescence. Four papers describe the applications of this technique to matrices as varied as reforming catalysts to lubricating oils.

The paper by *McElroy and Mulhall* takes a quite different approach from what we normally think of as petrochemicals applications, although their application is a vital link in refining crude oils to petroleum. They describe an XRF method for assaying the platinum, rhenium, and iridium content of fresh reforming catalysts. Because millions of dollars ride on a precise assay, an interlaboratory agreement of ±0.5% relative standard deviation between the catalyst supplier and purchaser must be achievable by the analytical technique used.

Sieber et al. then describe the determination of lubricant additive elements by XRF. When XRF alone is insufficient to obtain accurate information, complementary techniques such as ICPAES, AAS, and wet chemistry are also used. Agreement between results by different techniques enables an analyst to check the accuracy of the methods and provide customers with reliable data.

In the third XRF paper, *Shay and Woodward* describe the use of energy dispersive XRF for the determination of porphyrin complexed metals in petroleum and residua. These metals (V, Ni, and Fe) generally have a negative impact on refining operations and hence must be quickly and accurately determined. The authors describe the approaches used to eliminate the matrix effects and to correct for spectral interferences.

The fourth paper on XRF applications is by *Wheeler*. This paper also describes the energy dispersive XRF technique applied to crude and lubricating oils. For precise and accurate results to be obtained, proper excitation conditions, sample volume, and support film, an

adequate mathematical model for interelement corrections, and accurate standards are essential.

The final paper is by *Ohlson and Takahashi*. It describes a microcoulometric technique for the determination of trace amounts of halides, principally chloride, in hydrocarbons. Even though the combustion-coulometric technique is well established, certain types of heavy oils pose problems such as sluggish response due to refractory components, presence of heavy metals, and rapid aging of the quartz combustion tubes. This paper suggests a way to overcome these problems by changing the combustion tube design, adding copper oxide wire to the combustion outlet zone, and adding a post-combustion scrubber to remove deposits. There is certainly a need in the marketplace for an elegant and simple chlorine analyzer similar to those available for carbon, hydrogen, and nitrogen.

These papers provide the reader with the latest information on the state-of-the-art analytical instrumentation used for elemental analysis of petroleum products and lubricants. The major techniques used in this field are included here, although other techniques such as ion chromatography and microchemical analysis are missing.

I wish to acknowledge the prompt responses and cooperation received from the authors, reviewers, and the ASTM staff to make for a successful symposium and subsequent efficient publication of this volume. I also wish to thank the management of PARAMINS Technology Division, Exxon Chemical Company, for providing active support in my involvement in organizing the symposium and the subsequent book publication.

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A Review of Modern Instrumental Methods of Elemental Analysis of Petroleum Related Material: Part I—Occurrence and Significance of Trace Metals in Petroleum and Lubricants

ABSTRACT: Almost all elements in the periodic table are found in petroleum products, varying from percent levels for C-H-S to parts per million and parts per billion levels for transition metals. The presence of elements in crude oil is ascribed to its marine animal and vegetative origin. Compared with two other fossil fuels — coal and oil shale — petroleum is a lesser source of environmental pollution. Extensive data on crude oils composition are available. Determination of S, N, V, Ni, and Fe form an integral part of crude assay analysis of oils carried out by all oil companies. Generally it is agreed that V, Ni, and Fe occur as metallo-porphyrins; Hg, Sb, and As as organometallic compounds; Mo and Ge as carboxylic acid salts; and silica and NaCl as colloidal minerals.

The significance of metals either naturally present in crude and gasoline or purposely added to petroleum products is described. Trace metals in used lubricating oils indicate the wear performance of an engine, and can be used as a preventive maintenance check. A number of sample preparation schemes are necessary depending on the analytical technique to be used. This can vary from procedures as simple as dilution for XRF or AAS, to more involved procedures such as oxygen bomb combustion for ion chromatography, or wet ashing for AAS or ICPAES. Frequently, robots are used to speed sample dilution for XRF or ICPAES.

For quality assurance of these analyses, standard reference materials (SRMs) are used. At least three sources of these materials are Alpha Resources, Leco Corporation, and the National Institute of Standards and Technology. SRMs for crude oil, diesel oil, fuel oil, kerosene, lube oil, paraffin oil, and petroleum coke are currently available.

KEY WORDS: petroleum analysis, origin of elements in oil, wear metals, additive elements, standard reference materials, sample preparation

The main constituents of petroleum products are, of course, hydrocarbons; however, all crude oils, petroleum products, lubricants, and additives contain metals and nonmetals, either naturally occurring or deliberately added. A large number of elements in the periodic table have been found in the petroleum products varying from percent levels of carbon,

hydrogen and sulfur, to ppm and ppb levels of transition metals. A vast body of literature exists regarding the occurrence, significance, and analysis of metals and nonmetals in crude oils and petroleum products.

Part I of this paper will describe the occurrence and significance of metals found in petroleum products, while Part II will discuss applications of individual analytical techniques in this area.[2]

Occurrence of Metals in Crude Oil

Generally, it is believed that the source of petroleum is of marine animal and vegetative life deposited with sediment in the coastal waters in prehistoric times. Due to bacterial action over a period of time sulfur, oxygen, nitrogen, and volatile compounds evolved out of this material, but not completely. The end-product was a mixture of hydrocarbons containing varying amounts of sulfur, oxygen and nitrogen, and trace amounts of metals and other elements.

Unlike the two other fossil fuels, coal and oil shale, petroleum is a lesser source of elemental pollution in the environment. Unlike coal, which is burned unaltered as an energy source, oil is extensively processed in the refinery to yield a wide range of usable products.

Generally, sulfur and nitrogen are the most abundant elements in crude oils except for carbon and hydrogen. Sulfur up to 6 wt% and nitrogen over 1 wt% have been reported. More than 40 other elements are present in crude oils at trace levels (<1000 ppm); most common are: vanadium (up to 1000 ppm), nickel (up to 100 ppm), and iron (up to 30 ppm); in lesser amounts As, Be, Cd, Hg, Se, Cu, Sb, Ba, Cr, Pb, Mn, Mo, Te, and Sn have been found. Extensive data on elemental composition of crude oils can be found in Ref 1.

In general, the lowest metal containing U.S. crudes are from coastal and offshore fields of Texas and Louisiana. The highest metal containing U.S. crudes are found in California. A summary of worldwide crude oils is given in Table 1. Sulfur, nitrogen, vanadium, nickel, and iron are the most frequently determined elements in crude oils. There are probably millions of data points in this area, since these analyses are an integral part of "crude assay analysis" conducted by all oil companies. Most data, however, are considered proprietary. Some typical data on crudes from the world's giant oil fields are given in Table 2.

Presence of an unusual element, mercury, in crude oil from Cymric field of California's San Joaquin Valley has been reported [2]. The high level of mercury is attributed to its location on the southeast prolongation of the main mercury belt east of the San Andreas fault. Thus the cinnabar ore found in this region is saturated with hydrocarbons; and the crude oil hydrocarbons are saturated with mercury.

Ratios such as vanadium to vanadium + nickel and iron to vanadium are suggested as being useful for oil type characterizations [3]. Eleven North Alaskan oils derived from two genetically distinct source rock sequences were studied for their Cu, Fe, Mn, Ni, and V distribution. Both V-Ni and Ni-API gravity correlations were observed [3]. Since organometallic compounds are concentrated in the heavy ends of petroleum, transition element concentrations and ratios can serve as excellent oil–oil correlation parameters.

Generally, vanadium and nickel content increases with asphaltic content of crude oil (API gravity is an indicator). The lighter oils contain less metal [4].

The metals present in crudes can be divided into porphyrin and nonporphyrins. The former

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[2] This publication, pp. 19-51.

TABLE 1—*Worldwide crude oils* [1].

Country	Characteristics
U.S. (Texas, Louisiana)	Low metal, sulfur, and nitrogen content
U.S. (California)	High metal, sulfur, and nitrogen content
Canada (Alberta)	Similar to U.S. mid-continental
Canada (Western)	Medium-to-high sulfur and trace elements
Venezuela	Medium-to-high sulfur; high in vanadium and trace elements
Colombia	Low in sulfur and trace elements
Africa (Algeria, Libya, Nigeria, etc.)	Low in sulfur and trace elements; high nitrogen
Mid-East (Saudi Arabia, Iran, etc.)	High in sulfur; moderate trace elements
Indonesia	Negligible trace elements

have been the most extensively studied [4,5]. Yen [4] classifies all metals present in crude oils as follows:

1. Metalloporphyrin Chelates
   - Vanadyl and nickel porphyrins
   - Chlorophyll α and other hydroporphins
   - Highly aromatic porphin chelates
   - Porphyrin decomposition ligands
2. Transition Metal Complexes of Tetradentate Mixed Ligands (e.g., V, Ni, Fe, Cu, Co, and Cr)
   - Simple complexes from resin molecules
   - Chelates from asphaltene sheets
3. Organometallic Compounds (e.g., Hg, Sb, and As)
4. Carboxylic Acid Salts of Polar Functional Group of Resins (e.g., Mo and Ge)
**5. Colloidal Minerals** (e.g., silica and NaCl)

TABLE 2—*Elemental analysis of crude oils from giant oil fields* [1].

Country	S, wt%	N, wt%	V, ppm	Ni, ppm	Fe, ppm
Abudhabi	0.62–0.77	0.03	1	0.43	...
Algeria	0.02–0.31	0.01–0.09	0.2–1.5	...	...
Canada	0.2–3.67	0.02–0.12	<1–220	1–60	<1–629
Colombia	0.25–1.11	0.15	59–135	9–14	2–18
Egypt	0.84–2.06	0.08–0.18	15–120	7–72	58
Indonesia	0.07–0.18	0.12–0.34	...	7–33	...
Iran	0.76–3.68	0.02–0.3	11–151	3–39	...
Iraq	1.36–2.1	0.28	6–95	4–15	...
Kuwait	1.82–2.58	0.10–0.13	23–43	6–9	0.3–0.7
Libya	0.13–1.04	0.08–0.27	1–28	1–35	...
Nigeria	0.10–0.26	0.03–0.18	1-4	1-13	...
Saudi Arabia	1.25–3.91	0.03–0.34	6-80	1-20	...
United States					
Alaska (N. Slope)	1.07	0.23	16–30	4–13	...
Arkansas	0.9–2.1	0.02–0.11	12–19	4–23	1–6
California	0.2–1.2	0.1–0.77	1–403	2–174	2–125
Louisiana	0.1–0.8	0.2–0.08	0–4	0–6	...
Oklahoma	0.2–1.18	0.05–0.27	0–148	0–71	1–51
Texas	0.1–2.4	0.01–0.11	0–23	0–5	...
Wyoming	0.1–3.44	0.06–0.36	1–144	1–102	1–23

Using chromatographic separations, gel permeation chromatography, liquid chromatography, and neutron activation analysis, Filby [6] has shown that Fe, Co, Cu, Zn, Hg, Cr, and portions of Ni occur as non-porphyrin complexes. Arsenic and Sb appear to be present as low molecular weight compounds such as alkyl or aryl arsines and stibines.

Existence of metal complexes (called porphyrins) in fossil fuels was established by Alfred Treibs in the mid-1930s [7-10]. The concept of biomarkers in fossil fuels grew out of Treibs' pioneering work.

Porphyrins are a class of tetrapyrrole macrocyclics with a basic structural unit consisting of four pyrrole rings linked consecutively at the α positions by means of methine bridges (Fig. 1) [11]. The principal metal porphyrins in petroleum are Ni + 2 and VO + 2, although
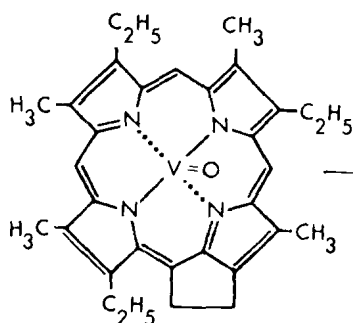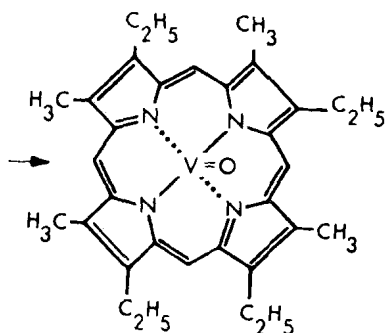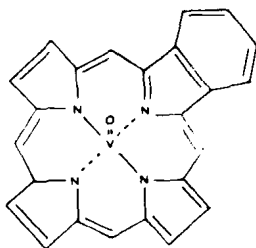
FIG. 1—Vanadyl porphyrins. (a) Deoxophylloerythroetiovanadyl porphyrin. (b) Ethiovanadylporphyrin. (c) Benzoporphin. (d) Porphin structure with two cycloalkano rings.

Cu + 2 porphyrins may be found in the early stages of sediment diagenesis [12]. Major chlorophylls and bacteriochlorophylls appear to be primary source materials of geopor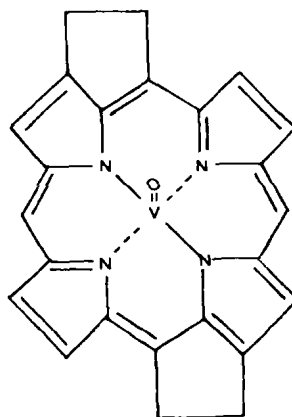phyrins found in the sedimentary systems. Metal chelation occurs during late diagenesis, predominantly by the fully aromatized porphyrin species. During catagenesis, which is the principal stage of oil generation from kerogen, the distribution and types of metalloporphyrins in the source rock undergo changes due to thermal effects. Metallation results in greater stability of the porphyrin macrocycle and in its preservation throughout the geological record [12]. Quirke [13] has hypothesized that the presence of metalloporphyrins in sediments requires good ion carriers which can complex with the cyclic tertrapyrroles to form metal complexes with high stability indices and stable metal-nitrogen bonds. This explains the predominance of nickel and vanadyl porphyrins in the geosphere.

A vast body of literature on metal petroporphyrins has been summarized in Refs 4, 5, 14, and 15.

An interesting suggestion regarding the presence of up to 0.1 wt% vanadium in some crude oils, particularly Venezuelan Boscan crude, has been to use the resid bottoms as a source of vanadium ore as a byproduct of petroleum refining [16,17].

Though tar sands are not strictly a part of crude oils, a brief mention of this topic is appropriate because of its analogous nature. Compared with high sulfur, metal-rich crude oil of the Venezuelan Boscan field, the vanadium content of most tar sand bitumens is relatively low (Table 3) [18].

If tar sand bitumens are residues of crude oils that have lost their light ends, it might be expected that metals, which are always concentrated in the heavier fractions of petroleum, would be present in greater amounts than are observed in these bitumens. Metalloporphyrin complexes of vanadium and nickel have been detected in some outcrop and shallow core samples. If these porphyrins are indigenous petroporphyrins, then these compounds can survive the weathering process. Metals in tar sands are always concentrated in the asphaltene fractions. Tar sand extracts high in sulfur usually have V:Ni ratios greater than 1, while those low in sulfur tend to have a V:Ni ratio of less than 118.

Significance of Metals in Petroleum Products

Trace metals in crude oil (Fe, Na, Ni, V, Pb, As) have an adverse affect on the refinery and processing operations, generally acting as catalyst poisons. Vanadium compounds damage the turbine blades and refractory furnaces. Sodium causes problems in furnace brickwork [20].

Complexity and expense of the refining operations increases tremendously as the sulfur content of crude oils increase from zero to several wt%. During distillation H2S is evolved and other sulfur compounds concentrate in the heavier distillation residue. The residual fuel

TABLE 3—*Composition of tar sand bitumen.*

	S, %	N, %	V, μmol/g	Ni, μmol/g
Boscan Crude	2.5	0.2	22	20
Tar Sands (Average of 7 from Wo., Utah, Calif., N.M., Alta)	3.0 (0.4–5.7)	0.7 (0.2–1.3)	2.2 (0.5–4.9)	1.3 (0.4–2.5)

oils with more than very small amounts of sulfur have to pay a price penalty in the marketplace. Some local, state, and federal environmental laws ban them altogether [20].

Branthaver [21] has reviewed the influence of metal complexes, particularly nickel and vanadyl, on various refining operations of crude oils. The effect on processing of heavy crudes is particularly serious.

The sulfur compounds are objectionable in refined solvents since they impart odor and may cause darkening of cooked varnishes and resins [20].

The sulfur oxides formed during gasoline combustion can be converted to acids which promote rusting and corrosion of engine parts, piston rings, and cause cylinder wall wear. Sulfur oxides emitted in exhaust are of course atmospheric pollutants [20].

In aviation gasoline, sulfur compounds have a deleterious effect on the antiknock efficiency of the alkyl lead compounds. If sulfur content was not limited, specified antiknock values would not be reached for highly leaded grades of aviation fuel. Some sulfur compounds corrode various metal parts of the engine system, with effects varying according to the sulfur compounds present [20].

In diesel fuels, vanadium can form low melting compounds (e.g., V_2O_5 melts at 691°C) and cause severe corrosive attack on all the high temperature alloys used in the gas turbine blades and diesel engine valves. For example, for AISI 310 steel, vanadium in fuel should be <2 ppm; at 10 ppm vanadium, the corrosion rate is thrice as high, and at 30 ppm level it is 13 times as much. However, if sufficient magnesium is present in the fuel, it will combine with vanadium to form higher melting compounds and reduce the corrosion [20].

Sulfur in diesel fuel causes wear due to the corrosive nature of the combustion byproducts, and increases the amount of deposits in the combustion chamber and on pistons. Low speed diesel engines can tolerate more sulfur than high speed ones [20].

High levels of sulfur in fuels adversely affect the carbon forming tendency in gas turbine combustion chambers, and large amounts of sulfur oxides in the combustion gases promote corrosion. Sodium and potassium combine with vanadium to form low melting eutectics (565°C), and with sulfur in the fuel to yield sulfates with melting points in the operating range of gas turbines. They produce severe corrosion. Hence sodium and potassium in the gas turbine fuels must be limited [20].

Calcium is not harmful from a corrosion standpoint; actually it helps to inhibit the corrosive action of vanadium. However, calcium can form hard bonded deposits which are not readily removed. Lead can cause corrosion and spoil the beneficial inhibiting effect of magnesium additives on the vanadium corrosion [20].

Ash forming metals found in the residual fuel oils are derived normally from the metallic salts found in crude oils. Of these, distillate fuels contain only negligible amounts, with the bulk ending up in the residual fuels. However, both distillate and residual fuels can pick up ash contributors during transportation from the refinery. In water transport in particular, fuel oils can be contaminated with sea water, dirt, scale rust, etc. Ash in heavy fuel oils can cause slagging or deposits and high temperature corrosion in boilers. It may attack the refractories in high temperature furnaces, kilns, etc., and it may affect the finished product in certain industrial processes such as ceramic and glass manufacturing [20].

High boiling range fractions and residual fuel usually contain higher amounts of sulfur, which creates corrosion and pollution problems. Conversion of sulfur to SO_3 during combustion and later reaction with water will form sulfuric acid, corroding the metal surfaces of equipment. Combining with sodium and vanadium complexes, sulfur forms deposits on the external surfaces of super heater tubes, etc., causing equipment corrosion and loss of thermal efficiency [20].

Antiknock additives are added to commercial gasolines to achieve the desired octane levels. The most widely used are tetraethyl and tetramethyl lead. Of course, in recent years,

lead is being phased out from gasoline due to environmental concerns and strict government restrictions. Methylcyclopentadienyl manganese tricarbonyl has been studied as one of the octane boosters.

Lubricants and Additives

Unlike the discussion above where the presence of naturally occurring elements in crude oil and refined petroleum causes mechanically adverse effects, a class of organometallic compounds are deliberately added to formulate better lubricants and additives. Generally, the presence of sulfur, chlorine, phosphorus, and alkaline earth metals define the composition of the lubricating oils. Though much of chemistry is proprietary, certain aspects are universal.

Naphthenates and alkyl aryl sulfonates of Ba, Cu, Co, W, Cr, and Fe are added to light fuel oils as combustion catalysts. Naphthenates of Ba, Ca, Mg, or Zn, carbonates of Ca and Mg, and sulfonate or chloride of Mg are added to heavy fuel oils as combustion catalysts, corrosion inhibitors, and antiground additives. Naphthenates or alkylaryl sulfonates of Cu, Fe, or Mn are added as a detergent dispersant component of antiground additives [*11*]. A summary of metal lubricants and additives generally used and their effects are given in Table 4 [*22,23*].

TABLE 4—*Lubricant and additive materials.*

Metal	Compounds	Performance
B	Borax and Esters	Antiwear agents, antioxidant, deodorant cutting oils, greases, brake fluids
Ba	Sulfonates, Phenates, Diorgano-diphosphates, Phosphonates, Thiophosphonates	Detergent inhibitors, corrosion inhibitors, detergents, rust inhibitors, ATF, greases
Ca	Sulfonates, Phenates	Detergent inhibitors, dispersants
Cd	Dithiophosphates	Steam turbine oils
Cr	Salts	Grease additive
Hg	Organic Compounds	Bactericide in cutting oil emulsions
Mg	Sulfonates, Phenates	Detergent inhibitors
Mo	MoS_2, Dibutyldithicarbamate, Phosphate	Greases, extreme pressure additives
Ni	Cyclopentadienyl Complexes	Antiwear agents, carbon deposit reduction, improved lubrication and combustion
P	Metaldialkyldithiophosphates	Detergents, antirusting agents
Pb	Naphthenate	Extreme pressure additive, greases, gear oils
Sb	Dialkyldithiocarbamates, Dialkyl-phosphorodithionates	Antiwear, extreme pressure, antioxidant
Se	Selenides	Oxidation and bearing corrosion inhibitors
Si	Silicone Polymers	Foam inhibitors
Sn	Organo Compounds	Antiscuffing additives, metal deactivators
Zn	Dialkyldithiophosphates, Dithio-carbamates, Phenolates	Antioxidant, corrosion inhibitors, antiwear additives, detergents, extreme pressure additives, crankcase oils, hypoid gear lubricants, greases, aircraft piston engine oils, turbine oils, ATF, railroad diesel engine oils, brake lubricants

Wear Metals in Used Oils

Trace metals in used lubricating oils come from the mechanical wear from oil-wetted components of an engine or as a contaminant from air, fuel, and liquid coolant. Generally, the metals are present as particulate materials rather than as true solutions. The presence of specific metals in the used lubricating oils is associated with specific metal components of an engine. In a normally running engine, wear metal content of the oil slowly increases due to normal wear. However, a sudden increase in one or more metal concentrations in oil indicates failure or excessive wear of a specific engine component. A large body of literature exists defining the analytical determination of wear metals in oils. Table 5 summarizes the typical wear metals and the type of engine wear they indicate [*11,23,24*].

Analysis of Petroleum Products

A vast body of literature abounds concerning the elemental analysis of crude oils, petroleum products, lubricants, and additives. As mentioned earlier, analysis of crude oils and used lubricating oils is an industry-wide standard practice. All the well-established elemental techniques (atomic spectroscopy, ion chromatography, microelemental analysis, neutron activation analysis, spark source mass spectrometry, and X-ray fluorescence) have been utilized for the analysis of petroleum products. It is beyond the scope of this review to exhaustively list all applications. Only typical examples to illustrate the applicability of various techniques will be given.

A number of monographs are available on the subject of elemental analysis of petroleum products [*4,19,25-27*]. Biennial reviews of the journal *Analytical Chemistry* cover the field of petroleum analysis in the odd years and are an excellent source of current literature in this field.

TABLE 5—*Wear metals in used lubricating oils.*

Metal	Wear Indication
Ag	Wrist pin bearings in railroad and auto engines, silver plotted spline lubricating pump
Al	Piston and bearings wear, push rods, air cooler, pump housings, oil pumps, gear castings, box castings
B	Coolant leakage in system
Cd	Bearings
Cr	Ring wear, cooling system leakage, Cr-plated parts in aircraft engines, cylinder liners, seal rings
Cu	Wear in bushings, injector shields, coolant core tubes, thrust washers, valve guides, connecting rods, piston rings, bearings, sleeves, bearing cages
Fe	Wear from engine block, cylinder, gears, cylinder liners, valve guides, wrist pins, rings, camshaft, oil pump, crankshaft, ball and roller bearings, rust
Mg	Cylinder liner, gear box housings in aircraft engines
Mo	Wear in bearing alloys and in oil coolers; various Mo-alloyed components in aircraft engines, piston rings
Na	Antifreeze leakage
Ni	Bearings, valves, gear platings
Pb	Bearings, fuel blowby, thrust bearings, bearing cages, bearing retainers
Sb	Crankshaft and camshaft bearings
Si	Dirt intrusion from improper air cleaner, seal materials
Sn	Bearings and coatings of connecting rods and iron pistons
Ti	Various Ti-alloyed components in aircraft engines
W	Bearings
Zn	Neoprene seals, galvanized piping