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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.

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.

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