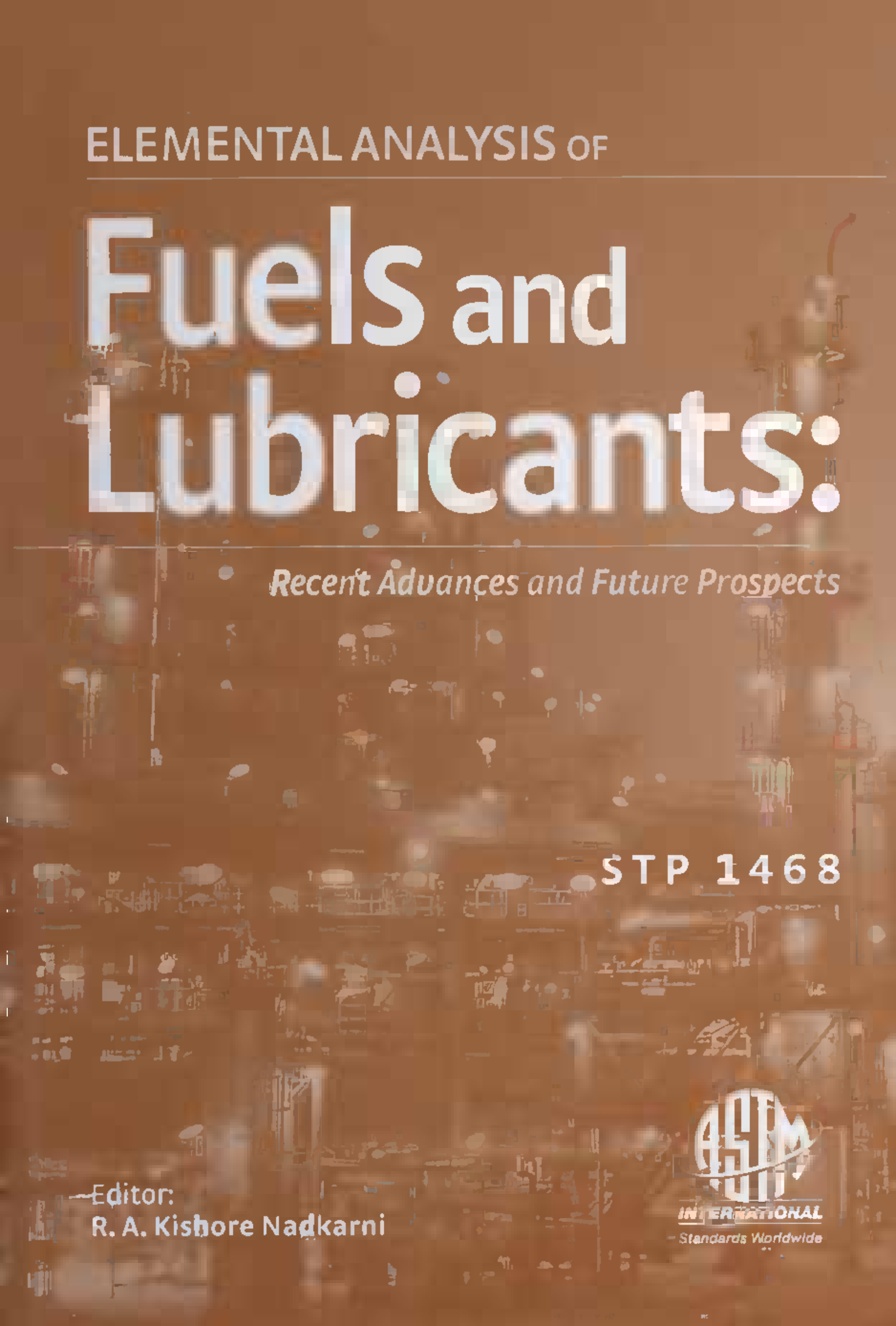

ELEMENTAL ANALYSIS OF

# Fuels and Lubricants:

*Recent Advances and Future Prospects*

STP 1468

Editor:
R. A. Kishore Nadkarni

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# *Elemental Analysis of Fuels and Lubricants: Recent Advances and Future Prospects*

*R. A. Kishore Nadkarni, editor*

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The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of the peer reviewers. In keeping with long-standing publication practices, ASTM maintains the anonymity of the peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM.

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# Foreword

This publication, *Elemental Analysis of Fuels and Lubricants: Recent Advances and Future Prospects,* contains selected papers presented at the symposium of the same name held in Tampa, Florida, on 6–8 December 2004. The symposium was sponsored by Committee D02 on Petroleum Products and Lubricants. The symposium chairman and editor was R. A. Kishore Nadkarni.

# Contents

# Overview

In spite of being a mature science, elemental analysis continues to play a vital role in product manufacturing and quality characterization in many sectors of all industries. Research divisions in both industry and academia continue devising new ways of lowering the elemental detection limits so that even the minutest amounts of elements in products could be determined in as accurate and precise a fashion as possible.

The ASTM International D02 Committee on Petroleum Products and Lubricants through its Subcommittee 3 on Elemental Analysis has played a large and crucial role in the last several decades in standardizing numerous elemental analysis methods used in the oil industry. Currently there are about 75 standard test methods under the jurisdiction of SC 3, and additionally at least 6 more are under active development and moving towards standard designations. I have no doubt that this activity will continue in the future. These standards comprise virtually all known modern techniques for elemental analysis of petroleum products and lubricants.

The first ASTM D02 symposium on this subject was held in New Orleans in December 1989 at which 20 papers were presented. Of these, 13 were published as a book, *Modern Instrumental Methods of Elemental Analysis of Petroleum Products and Lubricants, ASTM STP 1109.* The current and second "quindecennial" (i.e., every 15 years) was held in Tampa, Florida in December 2004. This was attended by over 120 people. Thirty papers were presented on diverse subjects from 64 authors from nine different countries: Brazil, France, Germany, Italy, the Netherlands, South Africa, Switzerland, U.K., and U.S. Of these, 12 papers were from the oil industry, 15 from the instrument manufacturers, 10 from national research organizations, and 4 from the universities.

The objective of this symposium and this book is to acquaint the readers with the latest advances in the field of elemental analysis and to focus on what avenues of future research to explore in this area. The subjects included are various elemental analysis techniques such as atomic absorption spectrometry, inductively coupled plasma emission and mass spectrometry, isotope dilution mass spectrometry, X-ray fluorescence, ion chromatography, gas chromatography-atomic emission detection, other hyphenated techniques, hetero-atom microanalysis, sample preparation, reference materials, and other subjects related to matrices such as petroleum products, lubricating oils and additives, crude oils, used oils, catalysts, etc.

Of the 30 papers presented at the symposium, 23 papers were published in the *Journal of ASTM International* (JAI), and are included in this ASTM publication. As far as possible, the papers have been arranged by analytical techniques used, although in some cases there is some overlap: ICP-AES, XRF, sulfur, mercury, other hetero-atoms.

The first article is from the plenary lecture given at the symposium by the symposium chairman Kishore Nadkarni. It covers total quality management practices advocated for obtaining a "perfect" analysis. Proper staff training, sampling, calibration and quality control practices, adherence to test method details, participation in proficiency testing, accreditation from national bodies, benchmarking, etc., are some of the critically important approaches that need to be taken to achieve the ideal state of analytical Zen perfection.

### Atomic Spectroscopy

Among the seven atomic spectroscopy papers in this book, five concern various aspects of ICP-AES, a technique widely used for the determination of metals in petroleum products and lubricants. *Onyeso* (*Ethyl Corporation*) presents an ICPAES method for the determination of additive elements and wear metals, principally manganese, in gasoline and diesel fuels, with simple dissolution in kerosene and using yttrium internal standard. Accessories such as direct injection nebulizer, ultrasonic nebulizer, chilled spray chamber, etc., were not necessary for this analysis.

*Fox* (*ExxonMobil Research and Engineering*) presents an ICPAES method for the determination of additive elements and wear metals in lubricating greases. Since such samples cannot be directly nebulized in the ICP plasma, alternate sample dissolution techniques were employed: dry sulfated ashing, microwave assisted dry ashing, microwave assisted acid digestion with both open and closed vessels. This method is being developed into an ASTM standard test method and is expected to be published by YE05. *Hwang and Leong* (*ChevronTexaco*) also discuss the use of microwave acid digestion for sample preparation before ICPAES measurements.

Elemental speciation using mass spectrometry in conjunction with ICPAES is a latest advance in atomic spectroscopy, which is becoming popular in analytical research labs. *Mason et al.* (*ExxonMobil Research and Engineering*) show how linking ICP-MS to various liquid chromatographic techniques has enabled determination of ppm levels of metals in hydrocarbons to ppb level measurements in refinery effluent streams. Hyphenated ICP-MS techniques were used to provide speciation information on nickel and vanadium in crude oils and assist in development of bioremediation options for selenium removal in wastewater treatment plants. Similar ICP-MS technique without sample demineralization was used by *Lienemann, et al.* (*Institut Francais du Petrole*) to determine the trace and ultra-trace amounts of metals in crude oils and fractions.

*Lukas et al.* (*Spectro Inc.*) describe an improvement made in rotating disc electrode atomic emission technology by incorporating a filter device in the rotrode, which enables to detect particles greater than 10 μm size.

*Tittarelli et al.* (*SSC, Milan*) employed a transverse heated filter atomizer with atomic absorption spectrometry to determine a number of trace elements in automotive and jet fuels. Sub-ppm detection limits were obtained. The use of filter furnace reduces the risk of elemental loss during drying and pyrolysis steps, and decreases the interferences due to molecular absorption and light scattering.

## X-Ray Spectroscopy

Similar to atomic emission spectroscopy, equally widely used technique for elemental analysis in the oil industry is X-ray fluorescence (XRF). There are four papers in this book using this technique, three of which deal with the determination of sulfur in gasoline and diesel.

*Wolska et al.* (*Panalytical BV*) compared performance of three XRF technologies: high power and low power WDXRFs and a bench top EDXRF. There are large differences in the sensitivities and hence varying lower limits of detection or qualification and sample throughput, for these technologies.

## Sulfur Analysis

One of the most important analyses done today on petroleum products, particularly gasoline, reformulated gasoline, and diesel, is for low levels of sulfur. Government regulations on sulfur emissions from automobiles and other combustion sources have steadily increased; hence, the increasing interest in devising precise and accurate methods for trace and ultratrace amounts of sulfur in fuels of the future as evident from seven papers on this subject published in this book.

*Nadkarni* (*Symposium Chairman*) reviewed the alternate methods available for sulfur determination in fuels. Out of about 20 ASTM standard test methods available, only about five (D 2622 WDXRF, D 3120 microcoulometry, D 5453 UV-fluorescence, D 6920 pyro-electrochemical, D 7039 MWDXRF) are appropriate for ultratrace amounts of sulfur in gasoline or diesel. However, in their actual industrial use only D 2622 and D 5453 predominate.

*Chen et al.* (*XOS Inc.*) describe a newly developed technology instrument based on monochromatic WDXRF for low sulfur analysis of fuels. The instrument has a significant advantage over existing WDXRF instruments in terms of increased sensitivity and improved signal to noise ratio. This technique has been recently given the ASTM designation D 7039.

Another new instrument recently developed for sulfur by XRF determination is described by *Wissmann* (*Spectro, Inc.*). This method uses polarized EDXRF, considerably reducing background scatter, and achieving detection limit comparable to that of WDXRF. Recent developments in detector technology and in closed coupled static geometry have resulted in further improvement of sensitivity for this application. This method is also in the developmental stage for ASTM method designation.

*Shearer et al.* (*Ionic Instruments and Dow Chemicals*) describe a novel technique developed for low levels of sulfur in hydrocarbon matrices using a low thermal mass temperature programmable and dual plasma chemiluminiscence detector. The method with appropriate modification can measure individual sulfur species similar to ASTM method D 5623.

### *On-line Sulfur Analysis*

Increasingly refineries, plants, and pipeline operators are focusing on obtaining quick turnaround for sulfur analysis rather than wait for time-delayed laboratory analysis. A large number of such installations are being operated in the industry around the world. Three papers in this book discuss applications of such on-line technology for sulfur determination in fuels. In an on-line application of X-ray transmission technology, *Fess* (*Spectro, Inc.*) describes the basis of this technology and its application to classification and blending of crude oils that contain between 0.1 and 3.3 m % sulfur. Commercial instruments based on this technology are being used in the field.

In a second on-line application paper, *Tarkanic and Crnko* (*Antek/PAC*) describe an on-line instrument based on ASTM Test Method D 5453, UV-Fluorescence Detection. The latter is a widely used method in the oil industry for low and ultra-low levels of sulfur. The on-line instrument appears to be very stable and fast ($<$ 1 min per analysis) over extensive periods of field operations.

In a third on-line application paper for sulfur analysis, *Rhodes* (*Rhodes Consulting*), ASTM Test Method D 6920 is applied for on-line application. This method uses pyro-combustion followed by electrochemical detection.

## Mercury Determination

Although adverse effects of mercury emissions on environment and humans has been known for decades, in recent years there has been concern regarding the mercury content of crude oils, and its emission through petroleum refining process. There are three articles in this book discussing this issue.

*Wilhelm et al.* (*Mercury Technology Services/EPA et al.*) provide a review of the presence of mercury in various parts of the world, its speciation, and alternate methods of determining low ppm and sub-ppm levels. *Fox et al.* (*ExxonMobil Research and Engineering*) describe a method for the determination of ppb levels of mercury in crude oils and distillation cuts using combustion cold vapor atomic absorption spectrometry technique. *Stockwell et al.* (*PS Analytical Ltd.*) describe the technique of atomic fluorescence spectrometry for the determination of mercury both before and after mercury removal from petrochemicals. The technique has been used for on-line measurements in installations operating around the clock for at least 2 years.

### Other Heteroatoms

*DiSanzo and Diehl* (*ExxonMobil Research and Engineering*) used GC-AED for the determination of elements such as carbon, nitrogen, sulfur, oxygen, and phosphorus in fuels and petroleum fractions. A simplified version of comprehensive GC × GC is coupled with atomic emission detector to reduce the hydrocarbon matrix interference using simple and rugged modulation along with rugged wide bore capillary columns. The technique together with other spectroscopic techniques such as GC-MS can provide information on many selected elements and compounds that may be present in fuels as additives or contaminants.

In a pair of papers, *Selby et al.* (*Savant, Inc. and Astaris LLC*) describe using phosphorus as an indicator of volatility of engine oils. Phosphorus is volatilized during Noack volatility test (ASTM D 5800). The volatile material is trapped and analyzed for total phosphorus using ICP-AES, and for phosphorus species using $^{31}P$ NMR spectroscopy.

An oxidative combustion followed by ion selective electrode detection method is proposed by *Nash* (*Antek/PAC*) for the determination of fluorine in fuels and lubricants. An ASTM method based on this technique is in development stage.

### Unpublished Symposium Papers

Some papers were presented at the Symposium; however, they were not submitted for publication by the authors. Nevertheless, they represent interesting approaches to some specific elemental analysis issues in the petrochemical industry. It would be useful if the authors eventually publish these articles for the benefit of others in the industry. These presentations include the following:

1. *Kelly et al.* (*NIST*) describe an isotope dilution thermal ionization mass spectrometry method for the determination of sulfur in fossil fuels. The method is being used in NIST for certification of a number of liquid fuels at low sulfur concentration levels.
2. *Kelly et al.* (*NIST*) also describe a "designer" calibration standard method for sulfur determination in fossil fuels for users to prepare NIST traceable working standards with known concentrations and uncertainties.
3. *Manahan and Chassaniol* (*Cosa Instruments and Dionex*) describe an oxidative combustion followed by ion chromatographic conductometric method for the determination of a number of nonmetallic elements such as sulfur and halogens in liquid and gaseous hydrocarbons. A standard based on this technique is under development in ASTM for designation as a standard method.
4. *Long et al.* (*NIST*) describe another method for mercury determination in crude oils using isotope dilution-cold vapor-inductively coupled plasma-mass spectrometry technique. The method has very high sensitivity, very low blank and high accuracy. The technique is being used to determine mercury in a large number of crude oil samples from Department of Energy strategic petroleum reserve in the mercury concentration range of 0.02–10 ng/g.

5. Finally, *Mason et al.* (*ExxonMobil Research and Engineering*) describe the approaches used for assay of fresh and spent reformer catalysts to determine the precious metals (platinum and rhenium) in them. Methods such as WDXRF, ICPAES, and classical wet chemistry methods are used for such analysis. Precise and accurate methods are critical for these analyses, since small errors in analysis can have a large impact in commercial transactions of these catalysts between the catalyst vendors and the oil companies.

Hopefully, the papers included here will provide the readers with the current state-of-the-art and future research trends in the field of elemental analysis in the oil industry. Most modern techniques used in the field are represented here.

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I want to thank various ASTM staff members (particularly David Bradley, Dorothy Fitzpatrick, Crystal Kemp, Hannah Sparks, and Roberta Storer) for their prompt response and cooperation that made the symposium and subsequent efficient publication in JAI and of this volume possible. My thanks are also due to the reviewers who did a very good job of providing technical reviews of all original paper submissions. Their invaluable assistance in reviewing the papers made the final publication a much better quality product.

*R. A. Kishore Nadkarni*
Chairman, D02.SC 3 and
Symposium Chairman

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