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# Standard Practice for
# Optimization, Calibration, and Validation of Atomic Absorption Spectrometry for Metal Analysis of Petroleum Products and Lubricants[1]

This standard is issued under the fixed designation D7740; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice covers information on the calibration and operational guidance for elemental measurements using atomic absorption spectrometry (AAS).

1.1.1 *AAS Related Standards*—Test Methods D1318, D3237, D3340, D3605, D3831, D4628, D5056, D5184, D5863, D6732; Practices D7260 and D7455; and Test Methods D7622 and D7623.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1318 Test Method for Sodium in Residual Fuel Oil (Flame Photometric Method)
D3237 Test Method for Lead in Gasoline by Atomic Absorption Spectroscopy
D3340 Test Method for Lithium and Sodium in Lubricating Greases by Flame Photometer (Withdrawn 2013)[3]
D3605 Test Method for Trace Metals in Gas Turbine Fuels by Atomic Absorption and Flame Emission Spectroscopy
D3831 Test Method for Manganese in Gasoline By Atomic Absorption Spectroscopy
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
D4628 Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry
D5056 Test Method for Trace Metals in Petroleum Coke by Atomic Absorption
D5184 Test Methods for Determination of Aluminum and Silicon in Fuel Oils by Ashing, Fusion, Inductively Coupled Plasma Atomic Emission Spectrometry, and Atomic Absorption Spectrometry
D5863 Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6732 Test Method for Determination of Copper in Jet Fuels by Graphite Furnace Atomic Absorption Spectrometry
D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories
D7260 Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants
D7455 Practice for Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis
D7622 Test Method for Total Mercury in Crude Oil Using Combustion and Direct Cold Vapor Atomic Absorption Method with Zeeman Background Correction
D7623 Test Method for Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption Method

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[1] This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

## 3. Terminology

3.1 *Definitions:*

3.1.1 *absorbance, n*—logarithm to the base 10 of the ratio of the reciprocal of the transmittance.

3.1.2 *atomic absorption spectrometry, n*—analytical technique for measuring metal content of solutions, based on a combination of flame source, hollow cathode lamp, photomultiplier, and a readout device.

3.1.3 *atomizer, n*—usually a flame source used to decompose the chemical constituents in a solution to its elemental components.

3.1.4 *blank, n*—solution which is similar in composition and contents to the sample solution but does not contain the analyte being measured.

3.1.5 *burner, n*—flame device used to atomize the analyte by burning in a high temperature flame mixed of a fuel and an oxidant.

3.1.6 *calibration, n*—process by which the relationship between signal intensity and elemental concentration is determined for a specific element analysis.

3.1.7 *calibration curve, n*—plot of signal intensity versus elemental concentration using data obtained by making measurements with standards.

3.1.8 *calibration standard, n*—material with a certified value for a relevant property, issued by or traceable to a national organization such as NIST, and whose properties are known with sufficient accuracy to permit its use to evaluate the same property of another sample.

3.1.9 *certified reference material, n*—reference material one or more of whose property values are certified by a technically valid procedure, accompanied by a traceable certificate or other documentation which is issued by a certifying body.

3.1.10 *check standard, n*—material having an assigned (known) value (reference value) used to determine the accuracy of the measurement system or instrument.

3.1.10.1 *Discussion*—This practice is not used to calibrate the measurement instrument or system.

3.1.11 *detection limit, n*—concentration of an analyte that results in a signal intensity that is some multiple (typically two) times the standard deviation of the background intensity at the measurement wavelength.

3.1.12 *dilution factor, n*—ratio of sample weight of the aliquot taken to the final diluted volume of its solution.

3.1.12.1 *Discussion*—The dilution factor is used to multiply the observed reading and obtain the actual concentration of the analyte in the original sample.

3.1.13 *graphite furnace, n*—electrothermal device for atomizing the metal constituents.

3.1.14 *hollow cathode lamp, n*—device consisting of a quartz envelope containing a cathode of the metal to be determined and a suitable anode.

3.1.15 *hydride generation, n*—device to atomize some metals which form gaseous hydrides.

3.1.16 *monochromator, n*—device that isolates a single atomic resonance line from the line spectrum emitted by the hollow cathode lamp, excluding all other wavelengths.

3.1.17 *nebulizer, n*—device that generates an aerosol by flowing a liquid over a surface that contains an orifice from which gas flows at a high velocity.

3.1.18 *NIST, n*—National Institute of Standards and Technology, Gaithersburg, MD. Formerly known as National Bureau of Standards.

3.1.19 *precision, n*—closeness of agreement between test results obtained under prescribed conditions.

3.1.20 *quality assurance, n*—system of activities, the purpose of which is to provide to the producer and user of a product, measurement, or service the assurance that it meets the defined standards of quality with a stated level of confidence.

3.1.21 *quality control, n*—planned system of activities whose purpose is to provide a level of quality that meets the needs of users; also the uses of such a system.

3.1.22 *quality control sample, n*—for use in quality assurance program to determine and monitor the precision and stability of a measurement system; a stable and homogenous material having physical or chemical properties, or both, similar to those of typical samples tested by the analytical measurement system.

3.1.22.1 *Discussion*—This material should be properly stored to ensure sample integrity, and is available in sufficient quantity for repeated long term testing.

3.1.23 *reference material, n*—material with accepted reference value(s), accompanied by an uncertainty at a stated level of confidence for desired properties, which may be used for calibration or quality control purposes in the laboratory.

3.1.24 *refractory elements, n*—elements forming difficult-to-dissociate oxides during combustion.

3.1.25 *repeatability, n*—difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long term and correct operation of the test method, exceed the values given only in one case in twenty.

3.1.26 *reproducibility, n*—difference between two single and independent results, obtained by different operators working in different laboratories on identical test materials, would in the long run, in the normal and correct operation of the test method, exceed the values given only one case in twenty.

3.1.27 *spectrometer, n*—instrument used to measure the emission or absorption spectrum emitted by a species in the vaporized sample.

3.1.28 *spectrum, n*—array of the components of an emission or absorption arranged in the order of some varying characteristics such as wavelength, mass, or energy.

3.1.29 *standard reference material, n*—trademark for reference materials certified by NIST.

## 4. Summary of Practice

4.1 An Atomic Absorption Spectrometer (AAS) is used to determine the metal composition of various liquid matrices.

Although usually AAS is done using a flame to atomize the metals, graphite furnace (GF-AAS) or cold vapor (CV-AAS) may also be used for metals at very low levels of concentration or some elements not amenable to flame atomization. This practice summarizes the protocols to be followed during calibration and verification of the instrument performance.

## 5. Significance and Use

5.1 Accurate elemental analysis of petroleum products and lubricants is necessary for the determination of chemical properties, which are used to establish compliance with commercial and regulatory specifications.

5.2 Atomic Absorption Spectrometry (AAS) is one of the most widely used analytical techniques in the oil industry for elemental analysis. There are at least twelve Standard Test Methods published by ASTM D02 Committee on Petroleum Products and Lubricants for such analysis. See Table 1.

5.3 The advantage of using an AAS analysis include good sensitivity for most metals, relative freedom from interferences, and ability to calibrate the instrument based on elemental standards irrespective of their elemental chemical forms. Thus, the technique has been a method of choice in most of the oil industry laboratories. In many laboratories, AAS has been superseded by a superior ICP-AES technique (see Practice D7260).

5.4 Some of the ASTM AAS Standard Test Methods have also been issued by other standard writing bodies as technically equivalent standards. See Table 2.

## 6. Interferences

6.1 Although over 70 elements can be determined by AAS usually with a precision of 1-3 % and with detection limits of the order of sub-mg/kg levels, and with little or no atomic spectral interference. However, there are several types of interferences possible: chemical, ionization, matrix, emission, spectral, and background absorption interferences. Since these interferences are well-defined, it is easy to eliminate or compensate for them. See Table 3.

6.1.1 *Chemical Interferences*—If the sample for analysis contains a thermally stable compound with the analyte that is not totally decomposed by the energy of the flame, a chemical interference exists. They can normally be overcome or controlled by using a higher temperature flame or addition of a releasing agent to the sample and standard solutions.

6.1.2 *Ionization Interferences*—When the flame has enough energy to cause the removal of an electron from the atom, creating an ion, ionization interference can occur. They can be controlled by addition of an excess of an easily ionized element to both samples and standards. Normally alkali metals which have very low ionization potentials are used.

6.1.3 *Matrix Interferences*—These can cause either a suppression or enhancement of the analyte signal. Matrix interferences occur when the physical characteristics – viscosity, burning characteristics, surface tension – of the sample and standard differ considerably. To compensate for the matrix interferences, the matrix components in the sample and standard should be matched as closely as possible. Matrix interferences can also be controlled by diluting the sample solution until the effect of dissolved salts or acids is negligible. Sometimes, the method of standard addition is used to overcome this interference. See 6.2.

6.1.4 *Emission Interferences*—At high analyte concentrations, the atomic absorption analysis for highly emissive elements sometimes exhibits poor analytical precision, if the emission signal falls within the spectral bandpass being used. This interference can be compensated for by decreasing the slit width, increasing the lamp current, diluting the sample, and / or using a cooler flame.

6.1.5 *Spectral Interferences*—When an absorbing wavelength of an element present in the sample but not being determined falls within the bandwidth of the absorption line of the element of interest a spectral interference can occur. An interference by other atoms can occur when there is a sufficient overlapping between radiation and emitted by the excited atoms and other absorbing atoms. Usually the bandwidth is much wider than the width of the emission and absorption lines. Thus, interferences by other atoms are fortunately quite limited in AAS. The interference can result in erroneously high results. This can be overcome by using a smaller slit or selecting an alternate wavelength.

6.1.6 *Background Absorption Interferences*—There are two causes of background absorption: light scattering by particles in the flame and molecular absorption of light from the lamp by molecules in the flame. This interference cannot be corrected with standard addition method. The most common way to compensate for background absorption is to use a background corrector which utilizes a continuum source.

6.2 *Standard Addition Method*—One way of dealing with some of the interferences in the AAS methods is to use a

**TABLE 1 Applications of AAS for Metal Analysis of Petroleum Products and Lubricants**

| ASTM Test Method | Matrix | Elements Determined |
|---|---|---|
| D1318 | Residual Fuel Oil | Sodium |
| D3237 | Gasoline | Lead |
| D3340 | Greases | Lithium and Sodium |
| D3605 | Gas Turbine Fuels | Calcium, Lead, Sodium, and Vanadium |
| D3831 | Gasoline | Manganese |
| D4628 | Automotive Lubricants | Barium, Calcium, Magnesium, and Zinc |
| D5056 | Petroleum Coke | Aluminum, Calcium, Iron, Nickel, Silicon, Sodium, and Vanadium |
| D5184 | Fuel Oils | Aluminum and Silicon |
| D5863 | Crude and Fuel Oils | Iron, Nickel, Sodium, and Vanadium |
| D6732 | Jet Fuels | Copper |
| D7622 | Crude Oils | Mercury |
| D7623 | Crude Oils | Mercury |

**TABLE 2 Equivalent AAS Test Methods**[A]

| Analysis | ASTM Standard | EI Standard | ISO Standard | DIN Standard |
|---|---|---|---|---|
| Lead in Gasoline | D3237 | IP 428 | 8691 | |
| Analysis of Gas Turbine Fuels | D3605 | IP 413 | | 51-790T3 |
| Additive Elements in Lube Oils | D4628 | IP 308 | | 51-391T1 |
| Al and Si in Fuel Oils | D5184 | IP 377 | 10478 | 51-416 |

[A] Excerpted from ASTM MNL44, *Guide to ASTM Test Methods for the Analysis of Petroleum Products and Lubricants*, 2nd edition, Ed., Nadkarni, R. A. Kishore, ASTM International, West Conshohocken, PA, 2007.

**TABLE 3 Elemental Analysis of Petroleum Products by AAS**

| Element | Wavelength, nm | Flame | Typical Detection Limits, mg/L | Matrix | ASTM Test Method |
|---|---|---|---|---|---|
| Aluminum | 309.3 | $N_2O + C_2H_2$ | 0.03 | Petroleum Coke; Fuel Oils | D5056; D5184B |
| Barium | | $N_2O + C_2H_2$ | 0.008 | Lubricants | D4628 |
| Calcium | 422.7 | $N_2O + C_2H_2$ | 0.001 | Gas Turbine Fuels; Lubricants; Petroleum Coke | D3605; D4628; D5056 |
| Copper | 324.8 | GF-AAS | 0.001 | Jet Fuel | D6732 |
| Iron | 248.3 | Air + $C_2H_2$ | 0.003 | Crude Oils; Fuel Oils | D5184 |
| Lead | 283.3 | Air + $C_2H_2$ | 0.01 | Gasoline; Gas Turbine Fuels | D3237; D3340 |
| Magnesium | 285.2 | $N_2O + C_2H_2$ | 0.00001 | Lubricants | D4628 |
| Manganese | 279.5 | Air + $C_2H_2$ | 0.001 | Gasoline | D3831 |
| Mercury | 253.65 | CV-AAS | 0.000008 | Crude Oil | D7622; D7623 |
| Nickel | 232.0 | Air + $C_2H_2$ | 0.004 | Crude Oils; Fuel Oils | D5863 |
| Silicon | 251.6 | $N_2O + C_2H_2$ | 0.06 | Fuel Oils | D5184B |
| Sodium | 589.6 | Air + $C_2H_2$ | 0.0002 | Residual Fuel Oil; Gas Turbine Fuels; Petroleum Coke; Crude Oils; Fuel Oils | D1318; D3605; D5056; D5863 |
| Vanadium | 318.34 | $N_2O + C_2H_2$ | 0.04 | Gas Turbine Fuels; Petroleum Coke; Crude Oils; Fuel Oils | D3605; D5056; D5863 |
| Zinc | 213.9 | $N_2O + C_2H_2$ | 0.0008 | Lubricants | D4628 |

technique called standard addition. IUPAC rule defines this technique as "Analyte Addition Method," however, the phrase "standard addition method" is well known and is widely used by the practitioners of AAS; hence, there is no need to adopt the IUPAC rule. This technique takes longer time than the direct analysis, but when only a few samples need to be analyzed, or when the samples differ from each other in the matrix, or when the samples suffer from unidentified matrix interferences this method can be used. The method of standard addition is carried out by: *(1)* dividing the sample into several (at least four) aliquots, *(2)* adding to all but the first aliquot increasing amount of analyte, *(3)* diluting all to the same final volume, and *(4)* measuring the absorbance, and *(5)* plotting the absorbance against the amount of analyte added. The amount of the analyte present in the sample is obtained by extrapolation beyond the zero addition. The method of standard addition may be less accurate than direct comparison; but when matrix interferences are encountered, it is necessary to use standard addition.

6.3 *Chemical Suppressants*—In some cases, ionization suppressors or other chemical reagents are added to the sample and standard solutions to suppress such interferences. Examples include: Test Method D3237 (lead in gasoline) uses iodine solution in toluene, Test Method D3831 (manganese in gasoline) uses bromine solution, and Test Method D4628 (additive elements in lubricating oils) uses potassium salt as ionization suppressant.

## 7. Apparatus

7.1 A simple schematic representation of AAS is shown in Fig. 1.

7.2 The basic AAS instrument consists of a suitable light source emitting a light spectrum directed at the atomizer through single or double beam optics. The light emitted by the source is obtained from the same excited atoms that are measured in the atomizer. The light leaving the atomizer passes through a simple monochromator to a detector. The measured intensity is electronically converted into analytical concentration of the element being measured. Quantitative measurements in AAS are based on Beer's Law. However, for most elements, particularly at high concentrations, the relationship between concentration and absorbance deviates from Beer's Law and is not linear. Usually two or more calibration standards spanning the sample concentration and a blank are used for preparing the calibration curve. After initial calibration, a check standard at mid range of calibration should be analyzed.

**HOLLOW CATHODE LAMP → NEBULIZER → FLAME → DETECTOR→**
**MONOCHROMATOR → PHOTOMULTIPLIER TUBE DETECTOR → RECORDER → PRINTER GRAPHICS**

FIG. 1 AAS Schematics

7.3 The ground state atom absorbs the light energy of a specific wavelength as it enters the excited state. As the number of atoms in the light path increase, the amount of the light absorbed also increases. By measuring the light absorbed, a quantitative determination of the amount of the analyte present can be calculated.

7.4 Two types of AAS instruments use either single beam or double beam. In the first type, the light source emits a spectrum specific to the element of which it is made, which is focused through the sample cell into the monochromator. The light source is electronically modulated to differentiate between the light from the source and the emission from the sample cell. In a double beam AA spectrometer, the light from the source lamp is divided into a sample beam which is focused through the sample cell, and a reference beam which is directed around the sample cell. In a double beam system, the readout represents the ratio of the sample and the reference beams. Therefore, fluctuations in the source intensity do not become fluctuations in the instrument readout, and the baseline is much more stable. Both types use the light sources that emit element specific spectra.

7.5 In AAS, the sample solution whether aqueous or non-aqueous, is vaporized into a flame, and the elements are atomized at high temperatures. The elemental concentration is determined by absorption of the analyte atoms of a characteristic wavelength emitted from a light source, typically a hollow cathode lamp which consists of a tungsten anode and a cylindrical cathode made of the analyte metal, encased in a gas-tight chamber. Usually a separate lamp is needed for each element; however, multi-element lamps are in quite common use. The detector is usually a photomultiplier tube. A monochromator separates the elemental lines and the light source is modulated to discriminate against the continuum light emitted by the atomization source.

7.6 *Burner System*—A dual option burner system consists of both a flow spoiler and an impact bead for optimal operation under different analytical conditions. Equivalent precision is obtained with the air–acetylene flame using the flow spoiler or the impact bead. However, for nitrous oxide–acetylene flame, noticeably poorer precision is obtained when using impact bead.

7.7 *Flame Sources:*

7.7.1 Usually, AAS instruments use flame as the atomization source. An air-acetylene flame is used for most elements; the nitrous oxide-acetylene flame reaches higher temperature (2300°C for air-$C_2H_2$ versus 2955°C for $N_2O$-$C_2H_2$), and is used for atomizing the more refractory oxide forming metals. Flame conditions used in AAS are summarized in Table 4.

7.7.2 Out of several possible combinations (Table 4), air-acetylene and nitrous oxide–acetylene are the most commonly used flames as atomization sources in AAS. Over 30 elements can be determined with the air–acetylene flame. The nitrous oxide–acetylene flame is the hottest of the flames used and produces a maximum temperature of 3000 °C. It can atomize refractory elements such as aluminum, silicon, vanadium, and titanium, and others, all forming highly refractory oxide molecules in the flame. Although nitrous oxide–acetylene flame can be used for the determination of over 65 elements, in practice it is used only where air–acetylene flame is ineffective.

7.8 *Hollow Cathode Lamps:*

7.8.1 A typical hollow cathode lamp consists of a quartz envelope containing a cathode, made of the element to be determined and a suitable anode. The sealed envelope is filled with an inert gas such as argon or neon at a low pressure. When a high voltage (up to 600 volts), is applied across the electrodes, positively charged gas ions bombard the cathode and dislodge atoms of the element used in the cathode. These atoms are subsequently excited and the spectrum of the chemical element is emitted. Hollow cathode lamps are preferred as the light sources because they generate a very narrow line, about one tenth of the elemental absorption line width. Usually these lamps are stable and can be used for several thousand determinations. By combining two or more elements of interest into one cathode, multi-element hollow cathode lamps are produced. For chemical elements which do not have close resonance lines and which are metallurgically compatible, multi-element hollow cathode lamps save the analyst considerable time not having to switch the lamps and recalibrate the instrument for the determination of multiple elements in the same sample.

7.8.2 Failure of hollow cathode lamps occur when the fill gas is gradually captured on the inner surfaces of the lamp, and finally, the lamp can no longer be lighted. Higher lamp current accelerates the gas depletion and cathode sputtering and should be avoided. It is a compromise between obtaining good sensitivity for the elements being determined and prolonging the lamp life.

7.8.3 Although hollow cathode lamps are an excellent, bright, and stable line source for most elements, for some volatile elements, where low intensity and short lamp life time is a problem, electrode-less discharge lamps can be used. The

**TABLE 4 Flame Conditions in AAS**

| Fuel | Oxidant | Temperature, °C | Burning Velocity, cm/s |
|---|---|---|---|
| Natural Gas | Air | 1700 to 1900 | 55 |
| Propane | Air | 1925 | 82 |
| Propane | Oxygen | 2800 | ... |
| Hydrogen | Air | 2100 | 320 |
| Acetylene | Air | 2300 | 160 |
| Hydrogen | Oxygen | 2550 to 2700 | 915 |
| Acetylene | Nitrous Oxide | 2955 | 180 |
| Acetylene | Oxygen | 3050 | 1130 |

latter are typically more intense than hollow cathode lamps, and thus offer better precision and lower detection limits for some elements.

7.9 *Nebulizers:*

7.9.1 Liquid sample is introduced into a burner through the nebulizer by the venturi action of the nebulizer oxidant. In its passage through the nebulizer, the liquid stream is broken into a droplet spray. During nebulization some liquids are broken into a finer mist than others. For example, MIBK is more efficiently converted into a fine droplet size than water. The nebulizer draws the solution up a tube of narrow diameter or capillary. High-viscosity fluids flow through the capillaries at a slower rate than the low-viscosity fluids. Hence, it is important to keep the viscosities of the samples and standards solutions similar to avoid the possibility of physical interference problems.

7.9.2 Nebulizer capillaries readily become clogged by particulate material and they sometimes corrode. It is very important to keep the particulate materials out of the nebulizers even though it may require a time-consuming filtration step.

7.10 *Monochromators*—A monochromator isolates a single atomic resonance line from the line spectrum emitted by the hollow cathode lamp, excluding all other wavelengths. A typical resolution in AAS for this discrimination is 0.1 nm band-pass. The light emitted by the spectral source is focused onto a narrow entrance slit. From this the light diverges until it reaches the first mirror where it is collimated into a parallel beam and directed towards the grating.

7.11 *Detectors*—A photomultiplier is used as a detector device in AAS because of its sensitivity over the range of wavelength used in AAS. The photomultiplier produces an electrical signal which is proportional to the intensity of the light at the wavelength which has been isolated by the monochromator. This electrical signal is then amplified and is used to provide a quantitative measure of absorption.

7.12 *Readouts*—The readout system of an AAS consists of a way to convert the electrical signal from the photomultiplier to a meter, a digital display, or a graphic printout. All modern instruments are capable of directly converting the signal to a metal concentration after inputting the sample weight taken for analysis, and a previously prepared calibration curve.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Base Oil*—U.S.P. white oil, or a lubricating base oil that is free of analytes, and having a viscosity at room temperature as close as possible to that of the samples to be analyzed.

8.3 *Organometallic Standards*—Multi-element standards, containing 0.0500 mass % of each element, can be prepared from the individual concentrates. Refer to Practice D4307 for a procedure for preparation of multi-component liquid blends. When preparing multi-element standards, be certain that proper mixing is achieved. An ultrasonic bath is recommended. Most laboratories use commercially available stock standards in either single or mixed element formats and at varying concentrations.

NOTE 1—Secondary standards such as those prepared from petroleum additives, for example, can be used in place of those described. If the use of such secondary standards does not affect the analytical results by more than the repeatability of this test method.

8.4 *Dilution Solvent*—A solvent that is free of analytes and is capable of completely dissolving all standards and samples. Mixed xylenes, kerosine, and ortho-xylene have been successfully used as dilution solvents.

## 9. Sampling

9.1 The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Thus, take lab samples in accordance with the instructions in Practice D4057 or D4177. The specific sampling technique can affect the accuracy of analysis.

## 10. Sample Handling

10.1 *Homogenization*—It is extremely important to homogenize the used oil in the sample container in order to obtain a representative test specimen.

10.2 *Ultrasonic Homogenization*—Place the used oil (in the sample container) into the ultrasonic bath. For very viscous oils, first heat the sample to 60 °C. Leave the sample in the bath until immediately before dilution.

10.3 *Vortex Homogenization*—As an alternative to ultrasonic homogenization, vortex mix the used oil in the sample container, if possible. For viscous oils, first heat the sample to 60 °C.

## 11. Preparation of Test Specimens and Standards

11.1 *Blank*—Prepare a blank by diluting the base oil or white oil tenfold by mass with the dilution solvent. Other dilution factors may be used as necessary.

## 12. Sample Introduction

12.1 Atomic absorption spectrometry can handle both aqueous as well as non-aqueous samples but AAS being a method for the analysis of liquids, if the sample to be analyzed is a solid or semi-solid, it needs to be brought into solution first. Some of the techniques used for such sample preparation include from simplest to more elaborate. Further discussion of sample preparation techniques used for the elemental analysis can be found in Practice D7455.

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[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

*(1)* Dilution of hydrocarbon liquid samples with organic solvents such as xylene, toluene, MIBK, kerosene, etc., for example, Test Method D3237, D3605, D4628, D5863, and D6732.

*(2)* Oxidation of organic liquid or solid samples in an oxygen pressurized stainless steel vessel, which converts the elements present to inorganic compounds. The contents are diluted with water or dilute acid for measurement.

*(3)* Incineration of organic samples with or without sulfuric acid followed by the dissolution of the residue in a mixture of acids or fusing with alkalies and further dissolution in a acid mixture, for example, Test Method D1318, D3340, D5056, D5184, and D5863.

*(4)* Dissolution in sealed PTFE (polytetrafluoroethlyene) pressure vessels with acids, heated for several hours at ~150 °C, and then dilution with water for measurement.

*(5)* Dissolution in a microwave oven in a mixture of acids in a very short period of time.

*(6)* Gold amalgamation before cold vapor measurement for mercury determination, for example, D7622 and D7623.

*(7)* Hydride formation of certain volatile elements – Se, As, Sb, etc. – and direct measurement by AAS.

*(8)* Incineration of organic samples by low temperature plasma. However, this takes several days to complete the oxidation. The residue is dissolved in a mixture of acids prior to AAS determination.

## 13. Calibration Standards

13.1 All AAS measurements of samples are preceded by calibration of the instrument with elemental standards. Such calibration need to be undertaken every time the flame is lit because each time the flame conditions cannot be precisely replicated and there will be small differences in the intensity of elemental lines with each flame condition. Such standards could be aqueous or organic solvent based. Aqueous metallic standards are used when samples are converted to aqueous acid forms, and organometallic standards in organic solvents are used in case where samples are simply dissolved or diluted in base oil or organic solvents. Generally the calibration standards are nowadays commercially available prepared in suitable concentrations. Either single element or multi-element standards are available.

13.2 The elements usually determined in petroleum products and lubricants are listed in Table 4 along with their recommended wavelengths, flame conditions, range of analysis and detection limits.

## 14. Procedure and Calculation

14.1 *Analysis*—Analyze the test specimen solutions in the same manner as the calibration standards (that is, same integration time, background correction points, flame conditions, etc.). Between test specimens, nebulize dilution solvent for a typical rinse time of 60 s. Calculate elemental concentrations by multiplying the determined concentration in the diluted test specimen solution by the dilution factor. Calculation of concentrations can be performed manually or by computer when such a feature is available.

14.2 *Quality Control with Check Standard*—Analyze the check standard after every fifth sample, and if any result is not within 5 % of the expected concentration, recalibrate the instrument and reanalyze the test specimens solutions back to the previous acceptable check standard analysis.

NOTE 2—To verify the accuracy and precision of the instrument calibration, certified standards such as NIST SRM 1085 (wear metals in oil) should be regularly analyzed.

## 15. Report

15.1 For each element determined, report the concentration in m% or mg/kg units as required in the product specifications. State that the results were obtained by using the specific test method utilized for that analysis.

15.2 If a concentration is determined to be below the detection limit (BDL) of the instrument, it should be identified as such (BDL) or less than (<) value along with the determined detection limit for that element.

## 16. Optimum Performance

16.1 In Table 5, suggestions to improve the precision and accuracy of metal analysis in petroleum products and lubricants using AAS are listed. These suggestions are based on practical laboratory experience and they should be a useful guide for the practitioners of this technique.

## 17. Quality Control

17.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

17.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample (see Practice D6299 and MNL7[5]).

17.2.1 Where possible, the C sample should not be the same as the one used for calibrating the instrument.

17.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total test process (see Practice D6299, Guide D6792, and MNL7[5]). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

17.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples is routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be periodically checked against the ASTM method precision to ensure data quality.

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[5] MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th ed., ASTM International.

TABLE 5 Practical Hints for Improved AAS Measurements

| Area | Improvement Suggestion |
|---|---|
| Sampling | Employ adequate mixing and sampling procedures, especially for heavy oils. Heat such oils sufficiently to obtain good fluidity, and then shake vigorously on a shaking machine. |
| Burner | Keep the burner clear of the optical path. Disassemble and clean the burner on a maintenance schedule that is appropriate for the frequency and the type of use. Monitor for deposit formation on the burner head and clean when necessary. |
| Nebulizer | Inspect the nebulizer tubing daily for kinks or cracks, and replace if necessary. Measure the nebulizer uptake rate daily to check for plugging. Clean the nebulizer if the rate is not normal. |
| Carbon Build-up | Adjust the gas flow rates when using the nitrous oxide/acetylene flame to minimize the carbon build-up on the burner. Clean off the carbon regularly during analysis with a sharp instrument. Carbon build-up can be particularly troublesome when nebulizing the non-aqueous solutions. |
| Gases | Prevent leakage of acetone from the acetylene gas tank by monitoring the pressure. Replace the tank when the pressure reaches 50 psi. |
| Hollow Cathode Lamps | Check the alignment of the hollow cathode lamps before analysis, so that maximum available light is directed along the optical path, following the manufacturer's instructions. Use correct lamp current. Select recommended band width. |
| Monochromator | Set the monochromator exactly to the wavelength peak approaching from the low wavelength side. Some elements have complex spectra; Be particularly careful with the monochromator adjustment for such elements, otherwise the instrument will be set on the wrong wavelength. |
| Glassware | Clean all glassware etc. to prevent contamination. Soak the glassware in warm dilute (5 %) nitric acid for several hours, and then rinse thoroughly with deionized water. |
| Blank Solution | Always run a blank with all solvents and other reagents added to the standards and the samples. |
| Reagents | Use pure analyte-free solvents. Verify that the solvents are indeed free of the analyte. |
| Sample Composition | If the oils contain viscosity index (VI) improvers, calibration standards also need to contain VI improvers. Alternatively, a large sample dilution will eliminate this effect. Match the matrix of standard solution to sample solutions as closely as possible. If ionization suppressant is necessary to add, do so for both samples and standards, in the same concentration levels. Maintain these concentrations when the samples are diluted. |
| Calibration Standards | Low level working calibration standards should be prepared fresh daily from higher concentration stock solution standards. |
| Calibration | Standardize the instrument each time the flame is ignited. Carry out calibration prior to each group of samples to be analyzed, or after change in any instrumental conditions. Keep all absorbances within the linear and calibrations ranges. Dilute the sample solutions gravimetrically, if necessary. |
| Check Standards | A single standard should be aspirated from time to time during a series of samples to check whether the calibration has changed. A check after every 5th sample is recommended. |
| Flame | The visual appearance of the flame serves as a useful indicator to detect change of conditions, perhaps as a build-up of carbon in the nebulizer or burner. To avoid flame transport problems, add a metal free base oil of about 4 cSt @ 100 °C to both samples and calibration standards. A 100 neutral base oil is suitable. |
| Background Correction | Whenever possible, employ background subtraction to obtain more reliable results. |
| Instrument | Verify the linearity of the concentration/absorbance response for each analyte following the instrument manufacturer's instructions. Perform all determinations within this range. Prepare the standard solutions with concentrations at the top of the linear range. |
| Standard Addition | This technique may be employed for samples known to have elemental or other interferences. |
| Bracketing Technique | For best results, use a bracketing technique for calibration involving taking absorbance readings for the calibration solutions before and after each of the sample solution measurements. |
| Multi-element Analysis | Since checking the absorbance of a sample is very quick once the instrument is calibrated for that analyte, but changing the wavelength settings and hollow cathode lamps takes longer time, it is economical to make measurements at a single wavelength on a series of samples and standards for an analyte before changing the conditions for the measurement of another analyte. |
| Quality Control | Establish and implement a QC protocol that can aid in achieving the required data quality. At a minimum, a QC sample should be analyzed with each set of samples analyzed. It is also important to plot this data on a QC chart. |

17.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the sample routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

17.6 It may be useful to confirm the optimum performance of the instrument system by analyzing certified reference materials such as available from NIST or other sources, if such materials are available.

17.7 Refer to relevant documents (see Practice D6299, Guide D6792, and MNL7[5]) for further guidance on QC and control charting technique.

## 18. Precision and Bias

18.1 Typical precision and bias obtained in the ASTM Standard Test Methods for petroleum products and lubricants are listed in Table 6. For most of these methods no bias can be calculated because of the lack of availability of standard reference materials.

## 19. Keywords

19.1 atomic absorption spectrometry; elemental analysis; fuels analysis; lubricant analysis

**TABLE 6 Precision of AAS Test Methods for Petroleum Products and Lubricants**[A]

| Test Method | Element | Matrix | Repeatability | Reproducibility |
|---|---|---|---|---|
| D1318 | Sodium | Residual Fuel Oils | 4 mg ⁄kg to 6 mg/kg | 9 mg ⁄kg to 23 mg/kg |
| D3237 | Lead | Gasoline | 1.3 mg/L | 2.6 mg/L |
| D3340 | Lithium | Greases | 0.014 $X^{2/5}$ | 0.075 $X^{2/5}$ |
| | Sodium | | 0.029 $X^{2/5}$ | 0.166 $X^{2/5}$ |
| D3605 | Vanadium | Gas Turbine Fuels | 0.452 $X^{0.5}$ | 0.616 $X^{0.5}$ |
| | Lead | | 0.244 $X^{0.5}$ | 0.900 $X^{0.5}$ |
| | Calcium | | 0.202 $X^{0.5}$ | 0.402 $X^{0.5}$ |
| | Sodium | | 0.232 $X^{0.5}$ | 0.738 $X^{0.5}$ |
| D3831 | Manganese | Gasoline | 0.3308 $(X + 0.1062)^{0.5}$ | 1.650 $(X + 0.1062)^{0.5}$ |
| D4628 | Barium | Lubricating Oils | 0.0478 $X^{2/3}$ | 0.182 $X^{2/3}$ |
| | Calcium | | 0.0227 $X^{2/3}$ or 0.032 | 0.0779 $X^{2/3}$ or 0.090 |
| | Magnesium | | 0.0168 $X^{2/3}$ | 0.0705 $X^{2/3}$ |
| | Zinc | | 0.0247 $X^{2/3}$ or 0.025 | 0.0537 $X^{2/3}$ or 0.048 |
| D5056 | Aluminum | Petroleum Coke | 15 mg/kg | 40 mg/kg |
| | Calcium | | 21 mg/kg | 36 mg/kg |
| | Iron | | 0.39 $X^{3.4}$ | 1.18 $X^{3.4}$ |
| | Nickel | | 1.27 $X^{0.5}$ | 1.69 $X^{0.5}$ |
| | Silicon | | 1.94 $X^{0.5}$ | 9.41 $X^{0.5}$ |
| | Sodium | | 0.19 X | 0.61 X |
| | Vanadium | | 1.19 $X^{0.5}$ | 2.93 $X^{0.5}$ |
| D5184 | Aluminum | Fuel Oil | 0.2968 $X^{2/3}$ | 0.7890 $X^{2/3}$ |
| | Silicon | | 0.3539 $X^{2/3}$ | 1.338 $X^{2/3}$ |
| D5863 | Nickel | Crude Oil | 0.20 $X^{0.65}$ or 0.005 $X^{1.4}$ | 1.3 $X^{0.53}$ or 0.06 $X^{1.2}$ |
| | Vanadium | | 1.1 $X^{0.5}$ or 0.13 $X^{0.92}$ | 0.33 $X^{0.90}$ or 1.20 $X^{0.80}$ |
| D6732 | Copper | Jet Fuel | $(X + 1)^{0.5}$ | 4.5 $(X + 1)^{0.5}$ |
| D7622 | Mercury | Crude Oil | 0.7147 $X^{0.60}$ | NA |
| D7623 | Mercury | Crude Oil | 0.4396 $X^{0.5864}$ | NA |

[A] NA: Not available
X: Average of two results
(a): Dependent on the analyte level