Designation: E1479 – 16

Standard Practice for Describing and Specifying Inductively Coupled Plasma Atomic Emission Spectrometers[1]

This standard is issued under the fixed designation E1479; 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 describes the components of an inductively coupled plasma atomic emission spectrometer (ICP-AES) that are basic to its operation and to the quality of its performance. This practice identifies critical factors affecting accuracy, precision, and sensitivity. It is not the intent of this practice to specify component tolerances or performance criteria, since these are unique for each instrument. A prospective user should consult with the manufacturer before placing an order, to design a testing protocol that demonstrates the instrument meets all anticipated needs.

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

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.* Specific safety hazard statements are given in Section 13.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E158 Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis (Withdrawn 2004)[3]

E172 Practice for Describing and Specifying the Excitation Source in Emission Spectrochemical Analysis (Withdrawn 2001)[3]

E416 Practice for Planning and Safe Operation of a Spectrochemical Laboratory (Withdrawn 2005)[3]

E520 Practice for Describing Photomultiplier Detectors in Emission and Absorption Spectrometry

3. Terminology

3.1 *Definitions*—For terminology relating to emission spectrometry, refer to Terminology E135.

4. Summary of Practice

4.1 An ICP-AES is an instrument used to determine elemental composition. It typically is comprised of several assemblies including a radio-frequency (RF) generator, an impedance matching network (where required), an induction coil, a plasma torch, a plasma ignitor system, a sample introduction system, a radiant energy gathering optic, an entrance slit and dispersing element to sample and isolate wavelengths of light emitted from the plasma, one or more devices for converting the emitted light into an electrical current or voltage, one or more analog preamplifiers, one or more analog-to-digital converter(s), and a dedicated computer with printer (see Fig. 1[4]).

4.1.1 The sample is introduced into a high-temperature (>6000 K) plasma that is formed from the inductive energy transfer to and subsequent ionization of the gas stream contained in the torch. The torch is mounted centrally in a metal structure, which is called the load coil. Energy is applied to the load coil by means of an RF generator.

4.1.2 The term inductively coupled refers to the fact that the physical phenomenon of induction creates a plasma by transferring energy from the load coil to the gas stream that has been momentarily preionized by a high voltage ignitor spark that functions only during plasma ignition.

4.2 When material passes through the plasma, it is vaporized, atomized, and partly ionized. The produced atoms and ions are excited into an energetically higher state. Free atoms and ions are excited from their ground states mainly by collision with the major plasma constituents. The excited atoms or ions subsequently decay to a lower energy state and emit photons, some of which pass through the entrance slit of

[1] This practice is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.20 on Fundamental Practices.

Current edition approved Nov. 1, 2016. Published December 2016. Originally approved in 1992. Last previous edition approved in 2011 as E1479 – 99 (2011). DOI: 10.1520/E1479-16.

[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.

[4] Courtesy of PerkinElmer, Inc., 761 Main Ave., Norwalk, CT 06859.

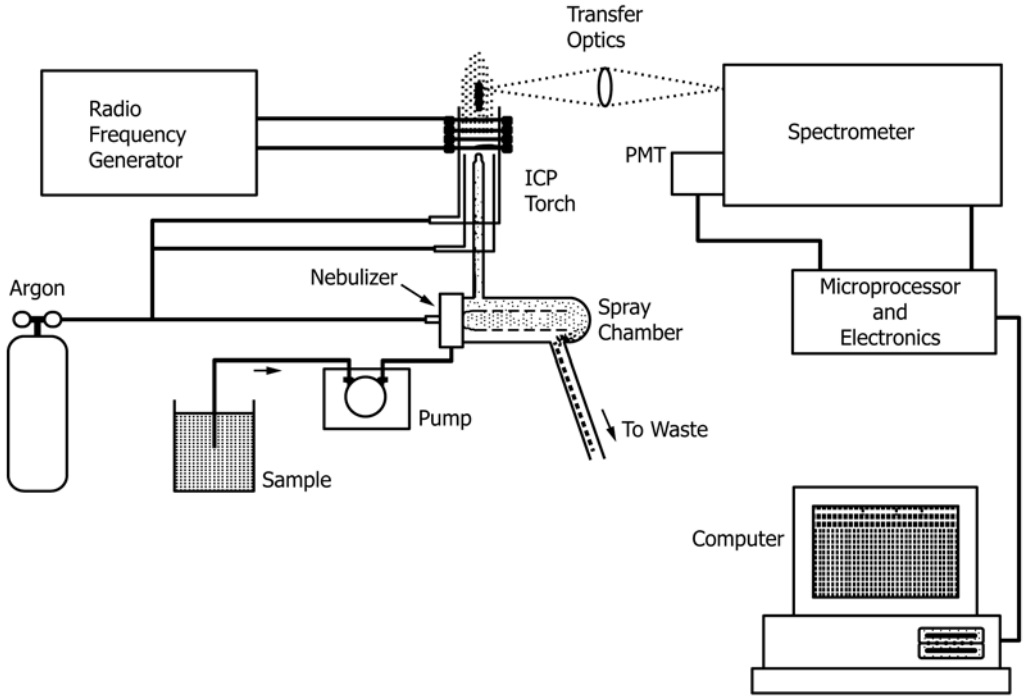

FIG. 1 Components of ICP-AES[4]

a spectrometer. Each element emits a unique set of emission lines. Photons of a desired wavelength may be selected from the ultraviolet and visible spectra by means of a dispersing element.

4.2.1 Instruments may determine elements either simultaneously or sequentially. The output of the detector generally is directed to a preamplifier, an analog-to-digital converter, and a computer which measures and stores a value proportional to the electrical current or voltage generated by the detector(s). Using blank and known calibration solutions, a calibration curve is generated for each element of interest.

4.2.2 The computer compares the signals arising from the various elements in the sample to the appropriate calibration curve. The concentrations of more than 70 elements may be determined.

4.3 Sensitivities (see 12.3) in a simple aqueous solution are less than 1 µg/g for all of these elements, generally less than 10 ng/g for most, and may even be below 1 ng/g for some.

4.3.1 Organic liquids may also be used as solvents with many yielding sensitivities that are within an order of magnitude of aqueous limits. Some organic solvents may afford detection limits similar or even superior to those obtained using aqueous solutions.

4.3.2 Direct sampling of solid materials has been performed successfully by such techniques as spark or laser ablation, by electrothermal vaporization and by slurry nebulization. However, these require greater care in the choice of reference materials and the operation of the sampling devices. Therefore, solid materials are usually dissolved prior to analysis.

5. Significance and Use

5.1 This practice describes the essential components of an ICP-AES. The components include excitation/radio-frequency generators, sample introduction systems, spectrometers, detectors, and signal processing and displays. This description allows the user or potential user to gain a cursory understanding of an ICP-AES system. This practice also provides a means for comparing and evaluating various systems, as well as understanding the capabilities and limitations of each instrument.

5.2 *Training*—The manufacturer should provide training in safety, basic theory of ICP-AES analysis, operations of hardware and software, and routine maintenance for at least one operator. Training ideally should consist of the basic operation of the instrument at the time of installation, followed by an in-depth course one or two months later. Advanced courses are also offered at several of the important spectroscopy meetings that occur throughout the year as well as by independent training institutes. Several independent consultants are available who can provide training, sometimes at the user's site.

6. Excitation/Radio Frequency Generators

6.1 *Excitation*—A specimen is converted into an aerosol entrained in a stream of argon gas and transported through a high temperature plasma. The plasma produces excited neutral atoms and excited ions. The photons emitted when excited atoms or ions return to their ground states or lower energy levels are measured and compared to emissions from reference materials of similar composition. For further details see Practice E172.

6.2 *Radio-Frequency Generator:*

6.2.1 An RF generator is used to initiate and sustain the argon plasma. Commercial generators operate at 27.12 or 40.68 MHz since these frequencies are designated as clear frequencies by U.S. Federal Communications Commission

(FCC) regulations. Generators typically are capable of producing 1.0 kW to 2.0 kW for the 27.12 MHz generator and 1.0 kW to 2.3 kW for the 40.68 MHz generator.

6.2.2 Generators more powerful than 2.5 kW are of limited practical analytical utility and are not commercially marketed with ICP spectrometers. The power requirements are related to torch geometry and types of samples to be analyzed. Refer to Practice E172 for details. More power (typically 1.5 kW to 2 kW for a 27.12 MHz generator utilizing a 20-mm outside diameter torch and 1.2 kW to 1.7 kW for a 40.68 MHz generator) is required for analyzing samples dissolved in organic solvents than is needed for aqueous solutions (approximately 1.0 kW to 1.4 kW). Less power is required for small diameter torches (for example, 650 W to 750 W for a 13-mm outside diameter torch).

6.3 *Load Coil:*

6.3.1 A coil made from copper (or another metal or alloy with similar electrical properties) transmits power from the generator to the plasma torch (see 7.6). A typical design consists of a two- to six-turn coil of about 1-in. (25-mm) diameter, made from ⅛-in. (3-mm) outside diameter and 1/16-in. (1.6-mm) inside diameter copper tubing (though larger tubing is used with two-turn coils). The tubing is fitted with ferrules or similar devices to provide a leak-free connection to a coolant, either recirculated by a pump or fed from a municipal water supply. Modern instruments also utilize air convection/radiation-cooled solid load coils, completely avoiding leak risks from liquid cooling.

6.3.2 Especially for liquid-cooled load coils, the high power conducted by the coil can lead to rapid oxidation, surface metal vaporization, RF arc-over and even melting if the coil is not cooled continuously.

6.3.3 A safety interlock must be included to turn off the RF generator in case of loss of cooling.

6.4 *Impedance Matching:*

6.4.1 To optimize power transfer from the generator to the induced plasma, the output impedance of the generator must be matched to the input impedance of the load coil. Some instruments include an operator-adjustable capacitor for impedance matching.

6.4.2 Alternately, RF frequency may be automatically tuned or varied in free-running fashion against a fixed capacitor-inductor network. However, most modern instruments incorporate either an automatic impedance matching network or a self-adjusting 'free running' RF generator to simplify ignition, to reduce incidence of plasma extinction when introducing sample solutions, and to optimize power transfer.

7. Sample Introduction

7.1 The sample introduction system of an ICP instrument consists of a nebulizer, a spray chamber, and a torch.

7.2 *Nebulizers:*

7.2.1 Samples generally are presented to the instrument as aqueous or organic solutions. A nebulizer is employed to convert the solution to an aerosol suitable for transport into the plasma where vaporization, atomization, excitation, and emission occur.

7.2.2 Some nebulizers, designated as self-aspirating pneumatic nebulizers, operating on the Venturi principle, create a partial vacuum to force liquid up a capillary tube into the nebulizer. Precision of operation may be improved if a peristaltic pump controls the solution flow rate.

7.2.3 Other nebulizers require an auxiliary device, such as a peristaltic pump, to drive solution to the nebulizer. Generally, pump-fed nebulizers are more tolerant of high levels of dissolved solids and much less affected by suspended solids and viscosity variations.

7.2.4 If fluoride is present in solutions to be analyzed, it is necessary to employ a nebulizer fabricated from HF-resistant materials (see 7.4.1.). It is possible to use the HF-resistant nebulizer for most other types of solutions, but sensitivity and precision may be degraded. An HF-resistant nebulizer may be more expensive to acquire and repair, and require greater operator proficiency and training than other nebulizers.

7.3 *Self-Aspirating or Non-Pump-Fed Nebulizers:*

7.3.1 *Concentric Glass Nebulizers (CGN):*

7.3.1.1 CGNs consist of a fine capillary through which the sample solution flows surrounded by a larger tube drawn to a fine orifice (concentric) slightly beyond the end of the central capillary (see Fig. 2). Minor variations in capillary diameter and placement affect optimal operating pressure for the sample gas flow and change the sample solution uptake rate. Uptake rates of liquid are typically 0.5 mL/min to 3 mL/min.

7.3.1.2 CGNs exhibit somewhat degraded sensitivity and precision for solutions that approach saturation or concentrations of more than a few tenths of a percent of dissolved solids. This problem can be greatly reduced by using an inner argon stream that has been bubbled through water in order to humidify the sample gas argon. Furthermore, since suspended solids may clog the tip, it is desirable to include a piece of capillary tubing of even smaller diameter in the sample solution uptake line. This action will isolate a potential clogging problem prior to clogging at the nebulizer tip.

7.3.2 *Micro-Concentric Nebulizer (MCN):*

7.3.2.1 To some extent, the MCN mimics the concept and function of the CGN but the MCN employs a thinner-walled poly-ether-imide capillary and TFE-fluorocarbon (or other polymer) outer body to minimize or eliminate undesirable large

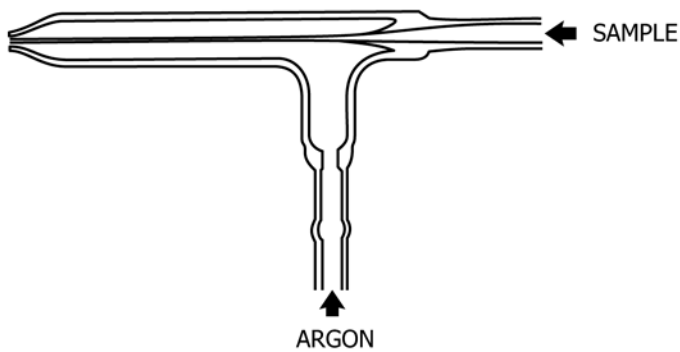

FIG. 2 Concentric Glass Nebulizer (CGN)[4]

drop formation and facilitate HF tolerance (see Fig. 3[4,5]). A true aerosol, as opposed to a mist, is produced consisting of only the desired smallest size droplets. Liquid uptake rates to produce similar sensitivity to CGNs are sharply reduced with the MCN. The MCN utilizes typical uptake rates of <0.1 mL/min and is HF tolerant. Unusually small sample size, low uptake rates, fast washout times, and very low drain rates characterize this nebulizer. The low uptake rate is particularly beneficial for extending limited sample volumes so that the long nebulization times encountered with sequential spectrometers performing multielement analysis may be successfully accomplished.

7.3.2.2 The initial purchase cost is higher for the MCN than for the CGN but the cost may be offset by a substantial reduction in recurring hazardous waste disposal cost (for example, heavy metal salts, mineral acids, etc.). This disposal cost reduction is because of the minimal waste volume inherent with low sample uptake rates and significantly reduced drain rates. In addition, micro-autosamplers that are compatible with the MCN are available for the optimum handling of small sample volumes.

7.3.3 *Cross-Flow Nebulizer (CFN)*—Consists of two capillaries held perpendicularly and with exit tips close together, as shown in Fig. 4. This nebulizer is preadjusted by the manufacturer and is known as a fixed cross-flow nebulizer. It requires little maintenance and is very durable. Problems with high levels of dissolved and suspended solids are similar to or less than those of the concentric glass nebulizer. Currently, for most analytical applications, the CFN is typically operated as a pump-fed nubulizer.

7.4 *Pump-Fed Pneumatic Nebulizers:*

7.4.1 *Grid Nebulizer*—constructed from a fine-mesh screen of acid and solvent resistant material, such as platinum, mounted vertically in an inert housing. Sample solution is pumped over the surface of the mesh. A high-velocity gas stream is directed through the openings in the screen, shearing the liquid from the wetted surface. A fine mist is produced and transported to the plasma. A second screen, parallel to the first

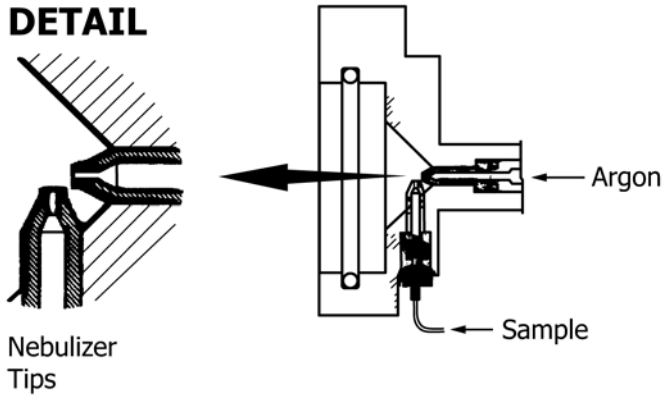

FIG. 4 Cross-Flow Nebulizer[4]

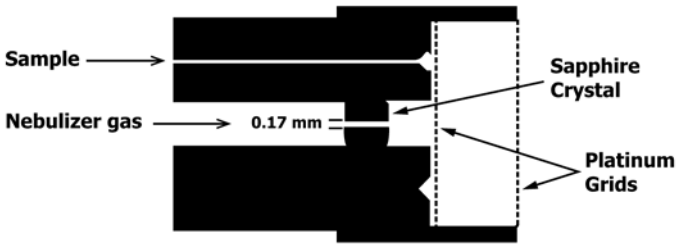

FIG. 5 Grid Nebulizer[6]

and mounted between the first screen and the spray chamber, is usually incorporated into the design to improve uniformity of droplet size and transport. A schematic diagram of a grid nebulizer is shown in Fig. 5.[6] The grid nebulizer may be employed to analyze fluoride-containing solutions, but an HF-resistant spray chamber and torch must also be used.

7.4.2 *Babington, Modified Babington or V-Groove Nebulizer:*

7.4.2.1 These nebulizers operate by passing an argon gas flow through a falling film of flowing analyte solution.[7] The falling film is typically guided by a shallow groove or channel to a pressurized argon orifice. Film thickness varies with channel depth, surface texture, cleanliness, and wettability (hydrophilicity), as well as liquid viscosity, surface tension, and sample delivery pump rate. The nebulizer does not aspirate naturally and must be pumped to fill the groove or channel with sample liquid.

7.4.2.2 This nebulizer can tolerate extremely high levels of dissolved and suspended solids, but some early versions of this device have developed a reputation for not being as sensitive or precise as a pneumatic or grid-type nebulizer. However, more recent versions easily perform as well as concentric or grid nebulizers. Most Babington nebulizers are HF-resistant. An example of a common arrangement is shown in Fig. 6. Alternate configurations may be used.

7.5 *Spray Chamber:*

[5] Courtesy of CETAC Technologies, a division of Transgenomic Inc., 5600 S. 42nd St., Omaha, NE.

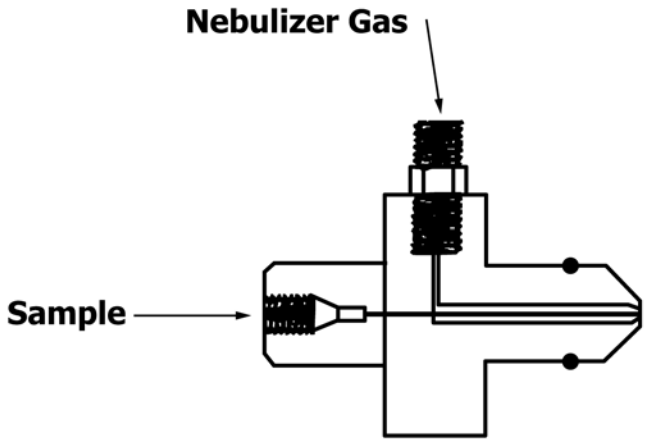

FIG. 3 Micro-Concentric Nebulizer (MCN)[4, 5]

[6] Courtesy of Leeman Labs, Inc., 110 Lowell Rd., Hudson, NH 03051.

[7] This nebulizer is sometimes misnamed a cross-flow nebulizer. It is most properly named a Babington or modified Babington nebulizer after the original and pertinent patent holder.

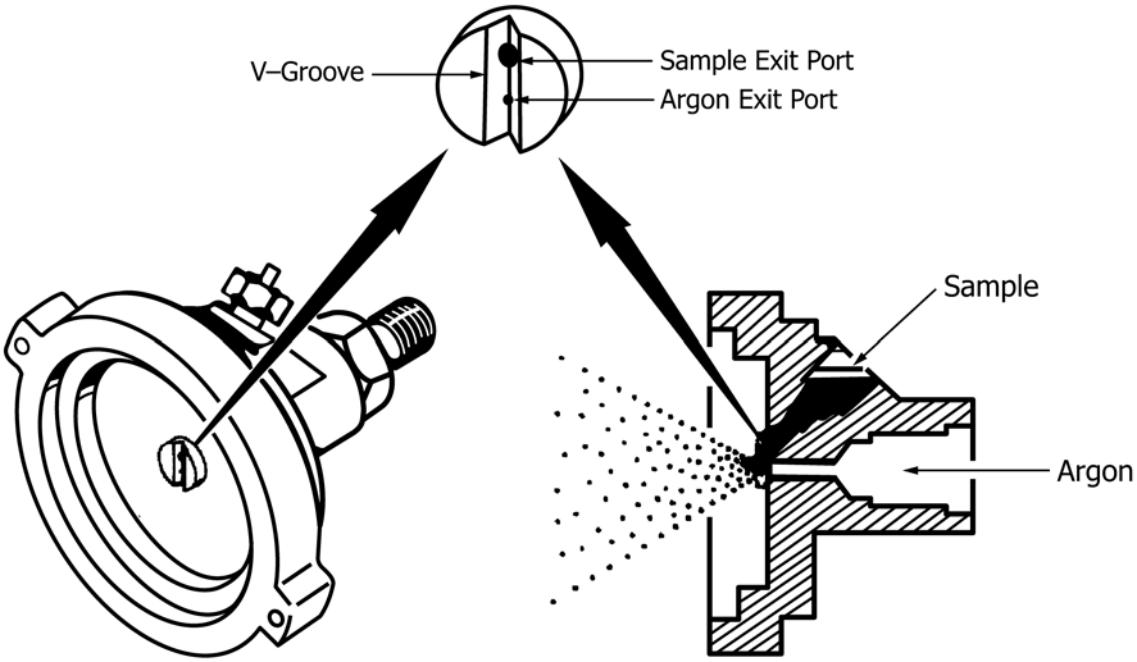

FIG. 6 Babington-Type Nebulizer[4]

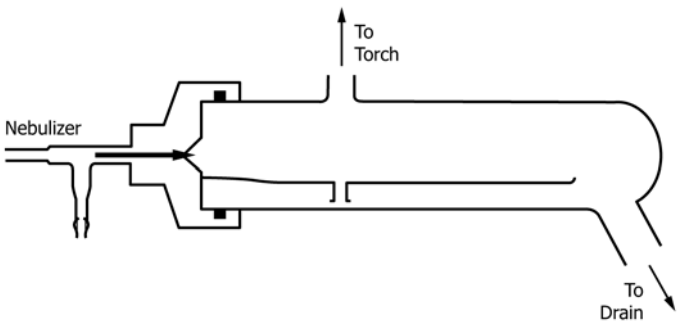

FIG. 7 Spray Chamber[4]

7.5.1 The spray chamber provides an aerosol droplet-sorting function to ensure that only the smaller droplets (typically less than 10 µm) reach the plasma. This ensures that the plasma is not significantly overloaded with solvent. The larger droplets are condensed and drained away from the spray chamber. If a peristaltic pump is used to remove the waste liquid from the spray chamber during nebulization, the pump tubing for the drain should be of a higher flow rating than that used for the intake.

7.5.2 A positive pressure must be maintained in the spray chamber to prevent air ingress and deliver the sample aerosol to the torch. Therefore, it is vital to ensure that all connections between the spray chamber and the ICP torch are leak-proof and that the drain plug is secure. If a peristaltic pump under computer control is incorporated, automatic start-up and shut-down can be achieved without depleting sample solution.

7.5.3 A common ICP spray chamber is a double-pass-type fabricated of glass (see Fig. 7). If fluoride is present in solutions to be analyzed, it is necessary to employ a spray chamber constructed from HF-resistant materials. It is possible to use the HF-resistant spray chamber for other types of solutions.

7.6 *Plasma Torch*—The argon gas that forms the plasma is directed through the load coil by means of a plasma torch.

7.6.1 The classic ICP torch is constructed of three concentric quartz tubes sealed together and is known as a 'one-piece' or 'fixed' torch (see Fig. 8[8]). These torches produce good plasma stability and are easy to use. However, they are, in general, not HF-resistant and, if damaged, the entire torch must be replaced.

7.6.2 The demountable torch (see Fig. 9[9]) is in common use particularly since the individual tubes can be replaced without replacing the entire assembly.

7.6.3 Alternate construction materials (typically ceramics) may be employed for analyzing solutions containing significant quantities of fluoride ion that attack quartz.

7.6.4 In place of quartz, fixed or demountable torches are commonly made of an HF-resistant ceramic. For demountable torches, all tubes, or often only the central or injector tube, are made from a corrosion-resistant ceramic.

7.6.5 If fluoride-containing solutions are to be analyzed routinely, the design and performance of the prospective manufacturer's HF-resistant torch should be evaluated.

7.6.6 There may be significant variations concerning installation and operation, and in costs of repair and maintenance.

7.6.7 Alternately, it may be possible to build an HF-resistant system or acquire one from a manufacturer different than the manufacturer of the spectrometer.

7.6.8 Before purchasing a third-party torch system, a demonstration of both repeated plasma ignition reliability and

[8] Courtesy of Spectro Analytical Instruments GmbH, Boschtr, 10 47533 Kieve, Germany.

[9] Courtesy of Texas Scientific Products (TSP), 11941 Hilltop Rd., Suite 15, Argyle, TX.

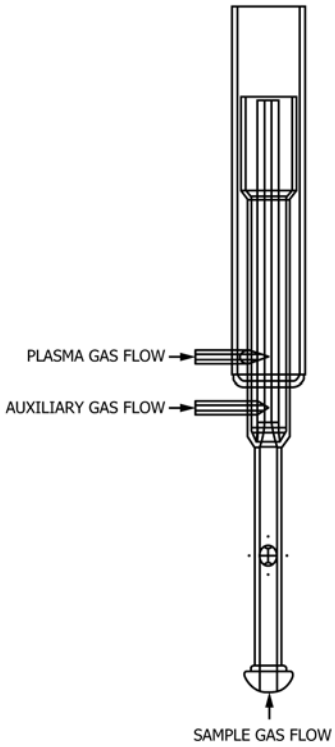

FIG. 8 Typical One-Piece Quartz Torch[8]

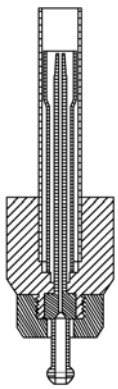

FIG. 9 Demountable Torch[9]

analytical performance with the fluoride medium in the intended model spectrometer is recommended unless a satisfactory guarantee of analytical performance and ignition reliability is obtained.

7.7 *Gas Flow:*

7.7.1 There are usually three gas flows through the torch. The first is the outer (coolant or plasma) gas flow which is directed tangentially to the internal surface of the largest diameter portion of the torch (typically 12 L/min to 20 L/min although some torches are designed to operate on much lower flow rates). Second, an intermediate (auxiliary) gas flow (typically 0.5 L/min to 1 L/min) is directed between the central tube through which the sample aerosol is introduced and the outer tube to reduce carbon formation on the injector tip when organic samples are being analyzed and to prevent the plasma from collapsing onto the injector tip. That intermediate flow, however, may also improve performance with aqueous samples. Third, an inner (sample or nebulizer) flow (typically 0.4 L/min to 1 L/min) passes through the sample introduction device and transports the analyte through the injector tip into the plasma. The manufacturer should provide data on optimal ranges for each of the gas flows since torch geometry strongly influences optimal rates.

7.7.2 An argon sheath attachment, a device for changing the flow rate of the intermediate flow during the analysis by introducing an additional argon flow under computer control, is available. This additional flow affects the observation zone that is viewed by the spectrometer and, consequently, for example, enhanced detection limits for the alkali metals and alkaline earths may be realized. Furthermore, the argon sheath attachment may also prevent salt encrustation in the inner tube with elevated salt concentration samples.

7.7.3 The inner gas flow rate is the most critical because it affects the injection efficiency and residence time of the sample in the plasma and, especially for a pneumatic nebulizer (see 7.3), influences transport efficiency of both analyte and solvent species. Both sensitivity and position of the maximum signal-to-noise ratio within the plasma are dependent on sample gas pressure and flow rate.

7.7.4 A conventional regulator and rotameter provide adequate stability in most cases, but a precision pressure controller, a mass flow controller (MFC) or a volume flow controller (VFC) may be required in certain applications. Accordingly, most modern instruments employ mass or volume flow controllers at least for the central or nebulizer flow or for all plasma gas flows. The intermediate flow affects the vertical location of the plasma relative to the torch and load coil. Gross variations will affect accuracy and precision. If available, the user should compare results with and without MFCs to determine their impact on performance.

7.7.5 In all but the most robust (all ceramic) torches, loss of outer gas flow through the torch will lead to rapid melting. A safety interlock must be included in the instrument design to turn off power to the RF generator in case of loss of argon pressure.

7.8 *Alternate Sample Introduction Devices:*

7.8.1 *Ultrasonic Nebulizer (USN):*

7.8.1.1 A USN with desolvation is the most generally useful alternate sampling device. In this device, the sample solution is pumped over the face of a quartz-coated crystalline transducer driven by a low-power RF generator (see Fig. 10). The apparatus is about ten times as efficient as the self-aspirating and pumped pneumatic nebulizers described in 7.3 and 7.4, respectively, and is useful for situations requiring very high sensitivity. Sensitivity is about ten times better with a USN than with self-aspirating and pumped pneumatic nebulizers. However, the USN device is more expensive and may require more maintenance than the pneumatic types.

7.8.1.2 Operation of the USN without desolvation is generally not practical because the large amount of aerosol reaching the plasma creates an excessive solvent load which reduces

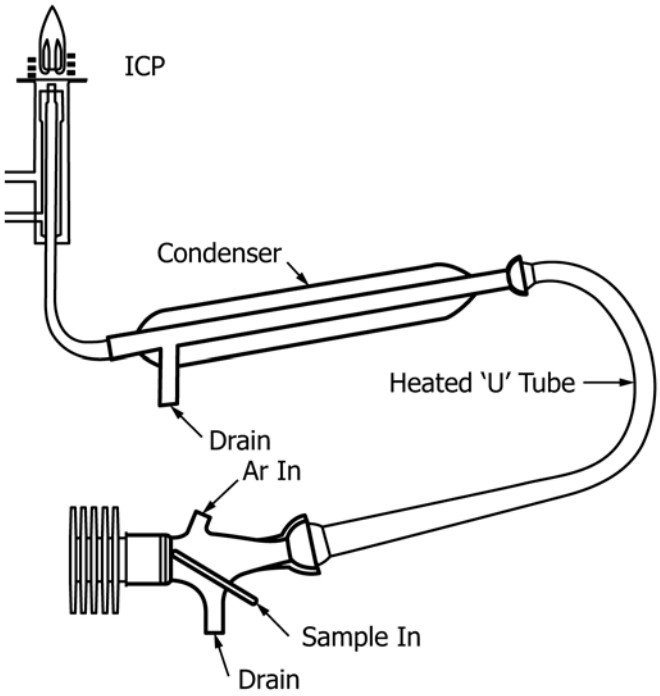

FIG. 10 Ultrasonic Nebulizer[5]

excitation efficiency and negates all potential sensitivity advantage. The aerosol, therefore, is passed through a heated zone followed by a condenser to limit solvent loading of the plasma.

7.8.1.3 Solutions with relatively high concentrations of dissolved solids or uncomplexed fluoride ion may not be suitable for ultrasonic nebulization.

7.8.1.4 Ultrasonic nebulizers may be slightly less stable than pneumatic nebulizers although USN performances of between 0.5 % RSD and 1 % RSD are typical with recent versions. The user should ensure that short-term precision (≤1 % RSD for raw, uncorrected, unratioed signals) and long-term drift rates are adequate for all anticipated applications.

7.8.2 *Hydride Generation:*

7.8.2.1 Hydride generation is useful for elements which may be converted to volatile hydrides. This technique affords improved sensitivity and avoids interferences arising from spectral overlap with non-volatile concomitants.

7.8.2.2 Interference occurs instead in the form of chemical inhibition of the hydride reaction. Concentrated transition metal or precious metal media or selected dissolved oxidants, or a combination thereof, produce the worst interferences. Combinations of metal and certain oxidants (notably, HNO_3 and its residues) can be particularly troublesome because of metal-induced catalytic effects which amplify the chemical inhibition. Optimization of reagent (reductant) concentration, generally lowering to the range between 0.5 % and 1 % $NaBH_4$ or less, can minimize or eliminate catalytic inhibition and frequently reduce the magnitude of interference to a range where standard addition or matrix matching become at least usable calibration schemes.

7.8.2.3 Take care to match samples and reference materials and to ensure that analytes are converted to the proper chemical form for quantitative conversion to the desired hydrides. Commercial equipment is available or the literature may be consulted to design and build a suitable apparatus. While hydride generation was performed in a transient manner in older atomic absorption systems, often the data acquisition systems of commercially available ICP-AES systems are more conducive to continuous generation.

7.8.3 *Electrothermal Vaporization (ETV):*

7.8.3.1 ETV may be employed where sample size is limited. As with hydride generation, the transient nature of ETV is not well suited to conventional ICP-AES data acquisition systems and may not work at all with many such systems. An efficient application of ETV usually requires a (fully) simultaneous ICP-AES instrument with a sufficiently high data rate (typically 10 Hz) for the ETV-generated transient analyte signals of interest. Accordingly, ETV is particularly unsuited to sequential spectrometer systems because relatively slow wavelength change between sequentially determined elements precludes any possibility of transient multielement ETV analysis on these systems. Because of extended dry and ash cycles, ETV systems have substantially slower cycling times in terms of sample throughput rate.

7.8.3.2 Autosamplers for ETV can be far more complex and expensive and might not be as readily available as they are for pneumatic nebulizers. Still, commercial systems allowing automatic ETV processing of up to 50 samples are available.

7.8.3.3 ETV precision is typically worse than that of gas nebulization and, therefore, requires a greater number of replicate determinations. Also, the interference effects are more intricate and extensive. The prospective user of ETV should try the desired analysis at the manufacturer's application laboratory before purchasing an instrument.

7.8.4 *Sampling Solid Materials*—Approaches to direct analysis of solid materials include insertion of a graphite rod containing the specimen into the plasma, arc or spark ablation, laser ablation, or slurry nebulization. Since considerable skill is required, these techniques cannot be recommended for the beginner or casual user. Commercial devices are available, but the prospective user should evaluate them critically before purchase to ensure that the required sensitivity, precision, and accuracy may be attained in the sample medium of interest. Considerable care is required in selecting appropriate reference materials for accurate calibration.

7.9 *Autosamplers*—For situations in which large numbers of similar samples are to be analyzed, an automated sample introduction system may be desirable. Such a device may be purchased from the manufacturer of the spectrometer or acquired from another supplier.

7.9.1 Two types of autosamplers are generally available. The simpler and less costly is a sequential device that processes samples in the sequence in which they are loaded into a rack prior to starting analysis. More sophisticated devices allow random access. This capability usually is coupled with an appropriate computer hardware/software system, or preferably directly integrated into the ICP-AES instrument software to allow recalibration if results for quality control check materials

are not within a specified range, or to repeat analyses if duplicates do not agree within acceptable limits of precision. If the user wishes to acquire an autosampler from a source other than the instrument manufacturer, the compatibility and software integration capability must be verified by consultation with the manufacturer of the spectrometer, and preferably by actual product demonstration.

8. Spectrometers

8.1 ICP spectrometers may be classified as sequential types, simultaneous types, a combination of the two called simultaneous/sequential systems, either employing a 'classical' photomultiplier tube (PMT) as detector, or a solid state detector. Most of the commercial instruments available currently utilize semiconductor solid state detectors, mainly in conjunction with simultaneous or simultaneous/sequential spectrometers, where the latter, for example, allows for the simultaneous detection of a certain wavelength interval around the analyte emission line(s) or even a larger spectral region.

8.1.1 *Sequential Spectrometers with PMT(s)*—Perform determinations by means of a monochromator and one or more photomultipliers. Commercially available instruments may select the wavelength to be monitored either by rotating the grating of the monochromator or moving the photomultiplier tube. Some spectrometers contain more than one monochromator or detector to improve rate of data acquisition or to optimize performance in each of several spectral regions, or both. In addition, a second monochromator may monitor a reference wavelength, thus permitting real-time internal standardization for improved precision.

8.1.2 *Simultaneous Spectrometers with PMT(s)*—Conventional simultaneous spectrometers usually employ one or more separate exit slits and photomultiplier tubes for each element of interest. A typical polychromator consists of an entrance slit, a diffraction grating, and exit slits located on the focal curve with a photomultiplier tube behind each exit slit. Alternatively, the exit slits and photomultiplier tubes may be replaced by a solid state detector (see 9.3). Some spectrometers have an auxiliary monochromator to allow determination of at least one additional element not detected by the array of photomultipliers mounted on the focal curve.

8.1.3 *Combined Spectrometers with PMT(s)*—Some photomultiplier tube-based instruments include each type of spectrometer described in 8.1.1 and 8.1.2. This design combines the advantages of the superior speed, excellent precision, and simultaneous multielement analysis attainable with a simultaneous instrument and the flexibility to measure the emission at any suitable ultraviolet or visible wavelength using a sequential scanning spectrometer.

8.1.4 *Solid State Detector Spectrometers*—Several, usually simultaneous, spectrometer designs can be combined with solid state detectors advantageously and are available commercially. Echelle spectrometers are available to provide high resolution in a compact x-y wavelength presentation format. The compact format allows imaging of the spectrum onto one or more silicon wafer array detectors including photodiode arrays (PDA), charge coupled device (CCD) arrays and charge injection device (CID) arrays containing anywhere from several thousand to over 250,000 individual pixels. Such advanced array detectors can theoretically be fitted with an image intensifier plate, but are typically operated at unity gain to control costs. Echelle-based spectrometers can either allow simultaneous 'full' spectrum capture or – in the form of an 'Echelle Monochromator'– the simultaneous capture of a small wavelength region around the analytical emission line of interest, typically sufficient for simultaneous background correction. Also, Echelle-based 'full spectrum' systems are commercially available that cover the relevant emission spectrum in, for example, two integrations, each consisting of about half of the full spectral range.

8.1.4.1 Spectrometers based on the Paschen-Runge Mount, with a single or several concave diffraction gratings and a number of linear solid state detector arrays arranged around the Rowland Circle to detect the wavelength dispersed radiation within a single diffraction order (usually the 1st only) reach a high and constant spectral resolution over large wavelength ranges. The lack of transmission optical components as, for example, a prism for order sorting, allows for deep UV spectral performance, down to 130 nm in some commercial intruments. Like Echelle systems, Paschen-Runge systems that capture the full spectral range in several (typically two) individual integrations also exist. Finally, solid state detector systems based on a Czerny-Turner Monochromator permitting the capture of the analyte emission and a certain wavelength interval around it simultaneously exist commercially.

8.1.4.2 Except for being used as a simultaneous spectrometer, solid state detectors have some distinct differences to other spectrometers.

8.1.4.3 For Echelle-based systems, the lack of detector gain above unity and the compact echelle format, which is characterized by the unusually short slit height required for prismatic order sorting collectively have an adverse effect on system sensitivity unless offsetting factors are introduced.

8.1.4.4 Successful offsetting (compensating) factors include various combinations of increased integration time (exposure time), detector cooling, improved spectrometer f/number (numerical aperture), and axial viewing of a horizontally oriented plasma torch.

8.1.4.5 Similarly for the other solid state detector spectrometer designs described and commercially available, an adaption of spectrometer and detector parameters, for example, demagnification of the diffraction plane image onto the light-sensitive detector part can offset the results from geometric and detector gain differences between PMTs and solid state detectors.

8.1.4.6 In at least one case, a combination of the above parameters consistently yielded routine sensitivity for an advanced array detector equaling that of photomultiplier tubes. This is also proven by the fact that the majority of ICP-AES instruments sold commercially currently utilize solid state detection, for the advantages described below.

8.1.4.7 An advantage of advanced array detectors is substantially larger numbers of simultaneously determined elements. In many cases two or more analytical spectral lines may be simultaneously monitored. Other advantages include: simultaneous background correction adjacent to every spectral line is

easily performed and offers potentially greater accuracy; alternate line selection provides more flexibility to minimize or avoid spectral interference, or to increase the overall system concentration dynamic range for a given element with both strong and weak lines are available for many elements, or both; availability of chemometric enhancement of signal to noise ratio using multiple lines of each element, including (full-spectrum) modelling approaches for spectral interference correction. Finally, the availability of a complete spectrum with each measurement opens the possibility for retrospective analysis, for example, detection of elements present in the sample not included in the original analytical program.

8.1.4.8 Short wavelength sensitivity inherently varies from one device type to the next and for many years was a severe limitation. Modern silicon wafer technology can improve poor UV photosensitivity limits by either elimination of the surface oxide dead layer during manufacture or by phosphor coatings. By either means, several systems are available with spectral response extending easily to wavelengths less than 167 nm, down to 130 nm.

8.1.4.9 Considerations in selecting an advanced array detector system should include spectral resolution, sensitivity for all elements of interest, particularly elements that give rise to short wavelength emissions, the number of available detector pixels, and the number of elements that can be simultaneously determined in the sample medium of interest. Often, the largest number of pixels does not guarantee the best results. Resolution sensitivity must be considered in the sample medium of interest.

8.2 *Spectrometer Environment:*

8.2.1 Temperature fluctuations affect instrument stability. Some manufacturers provide systems for maintaining a constant internal temperature within the optical compartment and sample introduction area provided that changes in the outside temperature are controlled within a specified range and rate of change. Other manufacturers design their spectrometers to be stable over a specified temperature range without attempting to control the spectrometer's internal temperature.

8.2.2 Changes in the refractive index of the atmosphere affect the optical path. Manufacturers provide various means to compensate for these changes, including use of evacuated (vacuum), sealed gas-filled, purged, or precise, pressure-controlled, gas-purged spectrometers, or use of optical compensation as follows:

8.2.2.1 Simultaneous instruments can be equipped with movable entrance slits or a rotating refractor plate behind the slit to shift the image of the entrance slit onto the exit slits. If equipped with a suitable 'full spectrum' detector (normally a solid state detector(s) array), simultaneous spectrometers may utilize a full-spectrum pattern matching algorithm to compensate for wavelength drift, using, for example, known emission line positions from a known reference sample or plasma background emissions (for example, Ar lines).

8.2.2.2 Sequential spectrometers may be designed to locate an intense reference line before each measurement and then, under computer control, make measurements at a predetermined wavelength distance from that reference line for each spectral line to be measured, or

8.2.2.3 The sequential spectrometer may be designed to move in turn to each approximate wavelength and perform a peak search before taking the measurement.

8.2.3 For all designs, it is necessary to provide internal temperature control, or to design and construct the spectrometer so that stability may be achieved without temperature control.

8.2.4 Since temperature and humidity changes may also affect the sample introduction system, detectors, and electronic readout, some manufacturing specifications may require that care be used in selecting a location for the spectrometer which experiences minimal variation in temperature and relative humidity. It is the responsibility of the user to provide a controlled environment as specified by the manufacturer.

8.3 *Optical Path:*

8.3.1 Since oxygen exhibits increasing absorbance with decreasing wavelength below 200 nm, the performance of an air path instrument degrades below that wavelength and generally is not useful below approximately 190 nm.

8.3.1.1 Purging the optical path with nitrogen or argon, or another gas with low absorption in the ultraviolet region may extend the spectral region to wavelengths less than 167 nm. Use of nitrogen as the purge gas is, in general, less expensive to maintain than vacuum path systems. Purge rates required to achieve a given performance level (below 200 nm) vary widely according to the manufacturing design of the spectrometer, volume to be purged, and the extent of leaks in the spectrometer housing. Before purchase, it is advisable to check the purge gas rate (L/min) required to achieve specified detection limits below 200 nm.

8.3.1.2 Alternatively, the spectrometer optical compartment may be purged with nitrogen or argon, sealed and maintained at a constant pressure. The nitrogen or argon is continuously filtered over reactive catalysts to scrub out oxygen and water. With modification to certain optical components in the spectrometer, wavelengths can be extended to 120 nm.

8.3.1.3 Vacuum path instruments are more expensive and require additional maintenance.

8.3.1.4 For purged, closed purged and vacuum systems, isolation of the optics from the laboratory environment will lengthen the useful lifetime of mirrors, gratings, and refractor plates (if present), especially if the environment contains significant concentrations of acid fumes.

8.3.1.5 If purging or vacuum are operated continuously, there is no effect on data acquisition rate once equilibrium has been achieved in the spectrometer. Alternatively, with proper design and construction, a vacuum spectrometer may include a feedback system to turn the vacuum pump on when an upper limit of about 10 Torr is exceeded and to stop the pump when a specified lower limit is achieved. Considering the total cost of operating a spectrometer for several years, the difference among vacuum, purge, and air-path spectrometers should be considered by assessing the costs of the required purge gas, of possible consumables or replacement parts, and possibly required periodic maintenance.

8.3.2 While most commercially available instruments are designed to collect radiation from the plasma directly, an acceptable alternative is the use of a fiber optic cable to

transmit radiation to the entrance slit of the spectrometer for wavelengths above 200 nm assuming the fiber optic wavelength cutoff does not negate the use of important analyte lines. Also, the cutoff wavelength may increase with age because of photodegradation. Photodegradation may also cause deterioration of the fiber optic itself requiring periodic replacement of the cable. It also may be necessary to clean the fiber optic periodically in accordance with the manufacturer's recommended procedure.

8.4 *Optical Systems:*

8.4.1 *Optical Dispersion*—The dispersing element in commercially available ICP spectrometers is commonly a diffraction grating, though some manufacturers use echelle gratings. For a given optical path, higher groove-grating densities or higher spectral orders, or both, provide better resolution but cover a narrower wavelength interval than gratings with lower densities. For any given grating, longer focal lengths provide better resolution but lower sensitivity (due to increased f/number). This may be offset by the use of a spectrometer with a larger diameter grating (that is, lower f/number) and by the diminution of spectral background and associated noise that arise from resolution improvement at wavelengths above about 220 nm.

8.4.1.1 Holographic gratings generally provide extended wavelength coverage and give rise to fewer ghosts, but mechanically ruled gratings provide adequate resolution and may exhibit higher intensity (due to greater peak reflectance).

8.4.2 *Overlapping Orders*—Filters or cross-dispersion prisms for echelle systems may be used to remove residual unwanted spectral orders. A prospective user should review carefully the types of analyses to be performed to ensure that an instrument with optimal grating density combined with spectral order(s), blaze and focal length is chosen. Resolution considerations are different for a sequential instrument than for a simultaneous instrument.

8.4.2.1 A sequential instrument allows flexibility in avoiding spectral interferences by selection of an alternative analytical wavelength. An alternative line may be less sensitive than the line of first choice, but if decreased sensitivity is acceptable, choosing such a line may avoid spectral interference.

8.4.2.2 In the case of simultaneous instruments, the optical geometry is fixed so that each detector receives photons at the exact sample wavelength for every analysis. More accurate mathematical corrections for spectral overlaps are possible. This is particularly true of solid state detector spectrometers that can simultaneously monitor background in multiple pixels adjacent to the spectral line.

8.4.2.3 In certain situations with PMT-based simultaneous systems, it may be desirable to install more than one analytical channel for element(s) to be determined in samples with differing and severe spectral overlaps. This is often inherant with solid state detector systems.

8.4.2.4 Another concern with a Paschen-Runge optical mount type (PMT-based) simultaneous instrument is that higher spectral order lines of concomitant species may give rise to spectral interferences. Installation of cutoff filters may be considered for polychromator-based systems to reduce overlap from higher order lines.

8.4.2.5 Solid state array detector based systems of any type are especially well suited for a multitude of analytical tasks. Weak-line (high concentration) analytical channels of major elements are often included to assess major element concentration and generate dual- or multiple-wavelength spectral interference correction for those trace analyte channels which are partially overlapped by interfering lines of the major elements in question.

8.4.3 To reduce cost, some sequential instruments are equipped with short optical paths or gratings with low groove density, or both. In contrast, other sequential instruments with higher groove density and focal length may have better resolution than echelle spectrometers. Take care, however, to ensure that resolution is adequate for all materials likely to be analyzed.

8.4.4 Some sequential instruments may be supplied with dual or composite gratings, that are interchanged by computer control, allowing the operator to select the resolution and spectral coverage required.

8.5 *Locating Wavelengths:*

8.5.1 A major concern in sequential instruments is the accurate location of the desired analytical wavelength. There are several methods employed to select the wavelength of interest, as follows:

8.5.1.1 One approach is to use a stepper motor to digitize the steps from a reference point to the wavelength of interest. For accurate results, wavelength calibration must be maintained. Frequent resetting of the reference point and temperature control of the spectrometer are required. Regular checks on the accuracy of wavelength settings should be performed to avoid changes resulting from wavelength drive wear. Some commercially available instruments include a means of maintaining the temperature in the optical path within a few tenths of a degree Celsius.

8.5.1.2 Another approach is to scan rapidly to the peak area and then scan that region to locate the center of the principal peak. This method is prone to error if interfering lines are present or if analyte concentrations are near the detection limit.

8.5.2 A potential user of a sequential instrument should require demonstration of the ability of the proposed instrument to provide acceptable accuracy, precision, and sensitivity for sample types of interest.

8.6 *Background Correction:*

8.6.1 Ion-electron recombination and stray radiation give rise to background continuum. Argon ion-electron recombination is a major component of the plasma background emission. Introduction of an aerosol into the plasma may affect the intensity of this background continuum. An additional recombination may also give rise to background continuum from dissolved major sample ions.

8.6.1.1 Provide background correction capability if an instrument is to be used to analyze samples for which matrix matched reference solutions do not provide adequate compensation for background shifts near analytical wavelengths. This situation is likely to be encountered if the major element

content is expected to vary significantly in samples analyzed in accordance with any one calibration scheme.

8.6.1.2 Background correction generally involves measuring the background emission at a wavelength near the analytical wavelength (free of line emission from concomitant elements) and subtracting that intensity from the total intensity measured at the analytical wavelength.

8.6.1.3 In some instances, if the background continuum intensity varies with wavelength, it may be necessary to measure the background on both sides of the analytical wavelength and interpolate to estimate the continuum intensity to be subtracted.

8.6.2 *Refractor Plate*—A quartz plate held between the entrance slit and the diffraction grating, perpendicular to the light path, on a rotating mount provides background correction on a polychromator. Under computer control, the refractor plate is rotated to direct background continuum into the exit slit, permitting a subtraction of background from the analyte signal.

8.6.3 *Entrance Slit Translation*—The entrance slit of a polychromator may be offset under computer control to observe selected areas of background continuum similar to the use of a refractor plate in 8.6.2.

8.6.4 *Wavelength Scans*—Some instruments, both simultaneous and sequential, allow display of peak profiles on a computer monitor and preparation of hard copy on an attached printer or plotter. To establish background correction parameters, it is necessary to record the signal from an analyte-free matrix solution and a matrix solution containing a typical concentration of each major element and analyte. For some cases, a one-point correction is adequate, while others may require averaging the values of two points bracketing the peak.

8.6.5 To maximize throughput and minimize drift errors, use as few correction points as possible. Note that spectral lines undergo concentration broadening. If a background correction point too close to the center of the peak is chosen, a portion of the analyte signal will be subtracted for analytes present at high concentrations, inducing an overcorrection error and creating non-linearity. Solid state detector based instruments typically provide a simultaneous measurement of at least a wavelength region including the analyte emission line and the surrounding background region. While the same rules and precautions apply for the choice of suitable background correction points and methods, the background correction itself has no influence on the throughput, as the region incorporating the analyte line, or the complete emission spectrum, is measured with every single integration. Thus, the use of a simultaneous solid state detector ICP-AES may significantly improve sample throughput and analytical efficiency compared to purely sequential systems.

8.6.6 If an analyte is to be determined only at levels one hundred times its detection limit or higher, background correction may not improve accuracy, since variations in background intensity may be insignificant relative to analyte signal. Consequently, the need for background correction decreases as concentration of analyte increases.

8.7 *Resolution and Spectral Coverage:*

8.7.1 The manufacturer should specify the resolution and spectral coverage of each monochromator in the instrument. Data obtained from elements with closely spaced doublets should be provided to verify the manufacturer's claim.

8.7.2 Some manufacturers offer an optional auxiliary monochromator to supplement the capabilities of a Paschen-Runge type polychromator. The operator may then determine elements for which the polychromator is not equipped.

8.7.2.1 The user should note that the background correction system employed for the polychromator portion of the instrument generally is not capable of correcting the auxiliary channel. It usually is necessary to identify a line without significant background, rather than attempt to measure and subtract the background signal from the total response.

8.7.2.2 The potential user of an auxiliary monochromator should evaluate the resolution, sensitivity, and wavelength coverage in relation to analytical requirements. Accessibility and ease of operation also should be considered. Some devices are mounted in areas that are difficult to access and are extremely difficult to optimize.

8.7.3 The manufacturer shall include software and hardware either for moving a refractor plate (8.6.2) or for adjusting the position of the entrance slit in the optical path (8.6.3) to optimize sensitivity and wavelength accuracy and to provide background correction measurement adjacent to the spectral line.

8.7.4 *Entrance and Exit Slit*—The width, height, and smoothness of slit edges will affect performance of the spectrometer. Instruments are available with either fixed, adjustable, selectable, or computer-adjusted entrance and exit slits. Fixed slits are less expensive but adjustable, selectable or computer-adjusted slits are often useful in increasing sensitivity. Increased slit width will provide more signal sensitivity but also more spectral background and less resolution. Slit selection is, therefore, often a tradeoff between resolution and sensitivity.

8.7.5 *Baffles*—If interferences from stray or scattered light are detected, baffles and masks (or other design components) may be installed. This often has been provided for in advance by the manufacture.

8.7.6 Together with detector capabilities as, for example, linear dynamic range, both resolution and spectral coverage of the dispersive system employed have an important influence on the overall analytical capabilities of the ICP-AES instrument under evaluation. In general, a large spectral coverage is desirable for the possibility to use additional emission lines, for example, in the low and vacuum UV portion of the spectrum (below 200 nm), in cases of spectral interferences or when matix components or non-metals (most of which have their most prominent emission lines in the low UV) are to be determined efficiently. Especially for simultaneous instruments with a solid state detector, which form the majority of the commercial systems today, spectral coverage has become less of a concern, due to the typically 'complete' coverage of the relevant ICP emission range. Tests for stray light influence or spectral overlaps, in the sample matrix of interest, allow for a check of the system's suitability for a concrete analytical task.

9. Detectors

9.1 Both conventional photomultiplier tubes and advanced electronic arrays such as CCD, CID and PDAs are used as detectors for ICP instrumentation.

9.2 *Photomultiplier Tubes:*

9.2.1 Photomultiplier tubes are used to convert photons to electrical current. Diffracted photons will pass through the exit slit and strike the photomultiplier tube positioned to detect them. The photons strike the active element of the photomultiplier giving rise to a cascading electron current, which is integrated by a capacitor. A computer records the accumulated voltage stored on the capacitor and this value is directly proportional to concentration of the analyte.

9.2.2 Some instruments are capable of integrating and zeroing the capacitor many times per second, which extends the dynamic range. Another approach uses a voltage-to-frequency converter combined with a counter to extend the linear range. Multiple order interferences may be minimized by selecting photomultiplier tubes that respond only in the spectral region of interest, such as solar blind tubes that respond to ultraviolet but not to visible radiation. For higher wavelengths, order filters may be placed in front of the PMT detector(s) except in the case of echelle spectrometers that employ cross-dispersion prismatic or secondary grating order sorting.

9.2.3 Select photomultiplier tubes with minimal dark current and noise, and high stability. Refer to Practice E520. Some manufacturers include provisions for adjusting PMT gain, either manually or under computer control, so that the useful concentration range may be varied. This provision is especially important for sequential instruments, since the photomultiplier tubes may be required to measure signals from elements with widely differing concentrations and sensitivities.

9.3 *Solid State Detector Arrays:*

9.3.1 Solid state detector arrays (CCD, CID, and PDAs, both in linear and two-dimensional (2D) form) are used in the majority of current ICP-AES instruments to generate electrical signals from incident photons. 2D arrays usually are employed with echelle gratings (in combination with either a cross-dispersion, order-sorting prism or diffraction grating) to achieve resolution equal to or better than that which can be obtained with conventional systems. Linear arrays are used, for example, with Rowland circle systems based on the Paschen-Runge mount. Both linear and 2D arrays offer the potential of simultaneous background correction. Line selection may be done after viewing data to avoid spectral overlaps and regions in which unacceptable large background shifts are encountered.

9.3.2 Use of a charge-coupled device (CCD) array, charge-injection device (CID) array or photodiode array (PDA) allows simultaneous determination of the entire spectral range, or selected segments thereof, making it unnecessary to vary the optical system to accomplish background correction. The techniques described in 8.6.2 and 8.6.3 require separate time intervals for background and analytical measurements.

10. Signal Processing and Display

10.1 *Signal Integration:*

10.1.1 The current from each detector (PMT or solid state detector arry) generally is amplified and integrated by electronic hardware. For PMTs, the amplified current may be integrated by a capacitor or integrating sample/hold circuit and the accumulated voltage measured one or more times during or after data acquisition. Array type semiconductor detectors are continuously integrating, but require additional control electronics (‘read-out system’, ‘camera’) for addressing the individual detector elements (pixels), to effect read-out and reset operations and process data. The capabilities of the integrator or control electronics, or both, often determine system capabilities. This is especially important for time-resolved measurements, for example, for transient sample introduction schemes such as ETV, FIA, or Laser Ablation.

10.1.2 The linear measurement range may be limited by self absorption in the plasma source, saturation of the photomultiplier tube or array detector, or saturation of the integrating electronics. While the linear range for each analyte is at least four orders of magnitude, solutions with concentrations beyond the normal range may be analyzed either by varying integration time, system gain or, for PMT based systems, a component change, which affects system gain. Range extension, however, reduces sensitivity. Inaccurate results will occur if emission at the wavelength of interest is so intense that the system no longer yields a linear response. For semiconductor array detectors, a phenomenon called ‘blooming’, the spill of signal from an intense analyte emission line into neighboring detector pixels (neighboring wavelength regions) may occur. Blooming can seriously affect the analytical capabilities of such a system in cases where a very small signal (trace) in the adjacency of a very large signal (matrix) has to be determined, up to a situation where the trace signal is completely masked by the ‘bloomed’ matrix line. Different solid state detector technologies are affected by blooming to different degrees and hardware and software-based anti-blooming measures are typically integrated in solid-state array detector based ICP-AES systems. A check of the anti-blooming capabilities with a suitable combination of matrix and trace element concentrations is recommended to assess system capabilities in the sample matrix of interest.

10.1.3 For PMT detectors, voltage-to-frequency converter may be used to produce a series of digital pulses with a frequency proportional to the amplifier output voltage, and the pulses accumulated on a counter. The integrated signal generally is read and stored by the instrument controller or computer. The manufacturer may include the hardware for signal integration and readout on one or more computer-addressable channel cards.

10.2 *Displays*—Displays may be analog, digital, or computer screen graphic in nature, or a combination thereof. Currently, ICP-AES instrumentation almost exclusively employs a dedicated instrument computer for instrument control, method and data display.

10.3 *Software:*

10.3.1 Software design is a major consideration in selecting an instrument. Numerous packages are available for interelement corrections, statistics, calibration, alignment, and creation of new routines. Some software packages include options such

as multi-dimensional spectral modeling, polynomial curve fitting, statistical weighting factors, use of an internal standard, automatic blank subtraction, and application of dilution factors to calculate results for solid or liquid samples which were diluted prior to analysis.

10.3.2 Different capabilities for formatting data for the user's needs and for providing results directly to customers are available. Storage and recall of multiple analytical methods including capability to automatically download stored values for many, if not all operating parameters and autosampler tray setup parameters, is a convenient feature provided by most manufacturers.

10.3.3 Wide variations exist in capabilities and ease of operation. Clarity and completeness of user's manuals are also significant considerations. The prospective user should visit an applications laboratory for each manufacturer of interest to perform a hands-on trial of the software before purchase.

10.4 *Computer Hardware*—Commercially available instruments generally include a dedicated computer. The user may acquire hardware from another supplier at lower cost, but must ensure that such equipment is compatible with instrumentation and software.

11. Interferences

11.1 Differences in viscosity, total dissolved solids, pH, surface tension, solvent volatility, and similar physical properties between sample and reference solutions may give rise to variations in transport efficiency.

11.2 The high temperature and electron density of the plasma give rise to a region of the plasma in which chemical matrix effects have little impact on emission intensities from the analytes when the plasma is viewed radially (side-on). Selecting optimal entrance slit dimensions and observing the emission at the proper height above the load coil minimizes such interferences in the radial view.

11.3 Axial (end-on) plasma viewing is very intense and can substantially improve sensitivity but is considerably more susceptible to matrix effects at normal nebulizer gas flows, greater than or equal to 0.8 L/min and plasma electron number densities, less than or equal to $2 \times 10^{15}/cm^3$.

11.4 High concentrations of easily ionized elements (mainly alkaline and earth-alkaline elements) in the sample shift the plasma neutral atom/ion+ free electron equilibrium, ultimately affecting the ratio between ionic and neutral atom emission lines. Accordingly, for the same analyte concentration in sample matrices of different easily ionized element concentration, different signals will be measured. This effect, accordingly termed 'easily ionized elements effect' (EIEE), is observable under both plasma observation modes (radial and axial view), but its magnitude is usually only relevant analytically for axially viewed plasmas, where it can lead to strongly non-linear calibration functions especially for the easily ionized elements and to large analytical errors. Strategies to reduce the EIEE include the use of radial viewing for the elements affected, or the addition of a suitable ionization buffer (typically CsCl) to all samples to match the overall easily ionized element concentration.

11.5 Potential spectral overlaps from concomitant elements may be estimated by measuring the signal arising from a high-purity single-element reference solution of the concomitant element. It is useful to consult tables of spectral lines to become aware of possible overlaps, especially when analyzing samples of unknown composition. If the overlap is severe, alternate line selection may be indicated to minimize spectral interference.

11.6 Potential interferences should be considered in the line selection process for traditional polychromators. With sequential instruments or solid state detector array systems, it may be desirable to select an alternate line, to avoid spectral overlaps even though sensitivity is usually lower. The analyst must be aware of the possibility of spectral overlap from an element that is not being determined. With traditional simultaneous instruments (polychromators), it may be necessary to install additional hardware to correct for concomitant elements or to allow determination of a given element at two or more wavelengths. Sequential instruments or solid state detector array systems permit measurement of other lines of interfering elements to allow correction of their contributions at the analytical wavelength.

11.6.1 The user must be aware of possible interferences from higher order spectral lines (for example, second or third order on Czerny-Turner monochromators) although their magnitude may be minimized by proper photomultiplier tube selection and by automated order-filter programming provided in some sequential systems, or general system design as in current solid state detector array based simultaneous systems of any type.

11.6.2 For the more common applications, spectrometer manufacturers typically employ staff who are experts on line selection. These technical personnel may well be more adept than many users at choosing the best lines for common applications for simultaneous, multiple-PMT based spectrometers. It is recommended that their suggestions generally should be accepted in finalizing the channels of a photomultiplier-based simultaneous spectrometer during the purchasing phase.

11.6.3 Refer also to 8.6 on background correction.

12. Performance Criteria

12.1 *Precision:*

12.1.1 Precision depends on the concentration of the element of interest, identity and concentration of concomitants, the type of sample introduction system employed, the adjustment and condition of any peristaltic pump tubing, the wavelength stability of the spectrometer, and the stability of the RF generator and gas control system.

12.1.2 Precision is directly related to the overall temperature gradient to which a variety of RF, optical, mechanical, nebulizer, detector, gas control, etc., components are subjected during the test period.

12.1.3 Short-term relative standard deviation (RSD) of ten consecutive measurements (raw, unratioed signal) of a suitable integration time (consult manufacturer's specifications) for elements of concentration at least fifty times the detection limit, in an acidified aqueous sample solution with no strong

interferences, should be less than 1.0 % for most elements with wavelengths greater than about 200 nm. The choice of integration time has an influence on the sample throughout and the user should ensure that the desired figures of merit and sample throughput can be achieved with the instrument in question, for example, via demonstration measurements.

12.1.4 Elements with lines near the upper or lower limit of the spectral range may show poorer precision. Since background correction requires measurement and combination of two or more signals on a sequential system, precision of background-corrected signals will be poorer on sequential systems when compared to uncorrected signals. Simultaneous measuring systems allow for acquiring the required signals simultaneously including simultaneous background correction, which overall can achieve improved precision.

12.1.5 Internal standardization (in which the analyte line signal is ratioed to the line signal of another added or indigenous element) can substantially improve precision. For further guidance on the use of internal standardization, refer to Practice E158.

12.2 *Sensitivity:*

12.2.1 Sensitivity can be estimated as a detection limit. The 3-sigma detection limit is defined in manufacturer's literature as the concentration of an analyte giving rise to a mean analytical signal three times the magnitude of the standard deviation of the blank. It is desirable to measure the detection limit using a reference solution containing analytes at concentrations approximating the values listed by the manufacturer to verify instrument performance. Contact the instrument manufacturer for their published detection limits.

12.2.2 Sensitivity depends upon many parameters, including the ionization and excitation potentials of the element, the dark current and stability in the case of a photomultiplier, detector and electronic background and noise for solid state detector systems, type of nebulizer employed, stability of gas flow and sample introduction system, RF generator stability, composition of solution, and duration of integration.

12.3 *Wavelength Selection:*

12.3.1 *For traditional polychromators equipped with PMTs:* When selecting the wavelengths to be utilized in a Paschen-Runge polychromator for particular applications, close collaboration between user and manufacturer is critical.

12.3.2 The physical size of photomultipliers and exit slit assemblies limits the proximity of adjacent analytical lines. This constraint may be partially alleviated by the use of mirrors and overhead photomultiplier sockets allowing orientation of photomultipliers perpendicular to each other, or by making some measurements using second or third order spectral lines, or both.

12.3.3 It may be desirable to incorporate two detectors for such elements, one for detecting a very sensitive line and the other for a line weaker by three orders of magnitude.

12.3.4 The manufacturer should provide detailed information on costs and downtime required to add one or more additional elements at the user's site. Array detectors may have full spectral coverage or may have, for example, over 200 pre-selected, permanently fixed lines. The pre-selected lines generally are chosen to minimize spectral interference for a wide variety of applications and typically provide at least one alternate line per element.

12.3.5 If the presence of high concentrations of concomitants causes spectral overlap, it may be desirable to select a less sensitive line to avoid spectral interferences. Lines with structured (rather than smooth) background should be avoided on channels used to measure concentrations that vary over a range of more than three orders of magnitude.

12.4 Analysts employing sequential or solid state array detector simultaneous instruments must select lines for the various analytes in each sample. Since selected lines must afford sensitivity appropriate for the required range of analyte concentrations, it may be desirable to use two lines of differing sensitivity. Line selection also should minimize the number and magnitude of spectral interferences from other analytes. Avoid lines with structured background emission.

13. Safety Features

13.1 *Internal Instrument Components:*

13.1.1 In general, and from applicable electrical safety regulations, any service, maintenance or repair of internal instrument components should only be performed by qualified personnel, normally from the manufacturer.

13.2 *Other (operational) Safety Concerns:*

13.2.1 *Torch Box*—In operation, the plasma produces extremely intense ultraviolet radiation, capable of causing severe eye damage. Refer to Practice E416. The torch box door should be interlocked so that power to the plasma is turned off if it is opened. This interlock also will prevent the possibility of the operator receiving an electrical shock from the load coil.

13.2.2 *Burn Hazard*—The plasma torch may become very hot, especially in cases of a malfunction. The operator should allow the torch to cool for several minutes before attempting to remove it. Even then, the torch should be handled cautiously to minimize the possibility of being burned in case it has not cooled sufficiently.

13.2.3 *Shielding*—The RF generator and torch box should be fully shielded in accordance with FCC and OSHA regulations to ensure that no excessive RF radiation escapes into the environment.

13.2.4 *Venting*—The plasma alone and the samples passing through the plasma give rise to airborne toxic substances. Also, large quantities of heat must be dissipated from the operation of some RF generators utilizing an RF power tube. This is usually less critical for solid state RF generators. The torch box and generator must be vented from the laboratory in an environmentally-acceptable manner. Refer to Practice E416.

13.2.5 *Liquid Waste*—Since much of a sample solution is rejected by the spray chamber, it must be collected and discarded in accordance with environmental regulations. Typically, licensed chemical waste disposal companies are contacted to remove the contents of spray chamber drain bottles. The user should ensure that any incompatible wastes are collected and stored in separate containers prior to ultimate disposal. Refer to Practice E416.

13.2.6 *Emergency Shutdown*—The instrument must be equipped with safety interlocks to turn off power in case the cooling fluid (water for liquid-cooled or air for air-cooled

systems) or argon flow rate falls below acceptable levels. The generator should shut down automatically if cooling air flow decreases below a rate adequate for cooling operating components. The generator must also shut off automatically if reflected power exceeds amounts allowing for safe operation.

13.2.7 *Additional Information*—For specific details concerning safety procedures, consult Practices E416.

14. Keywords

14.1 ICP-AES; optical emission; spectrometry, atomic emission; spectroscopy, emission; spectroscopy, inductively coupled plasma