Designation: E406 – 81 (Reapproved 2012) E406 – 19

Standard Practice for Using Controlled Atmospheres in Spectrochemical AnalysisAtomic Emission Spectrometry[1]

This standard is issued under the fixed designation E406; 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 general recommendations relative to the use of gas shielding during and immediately prior to specimen excitation in opticalatomic emission spectrochemical analysis. It describes the concept of excitation shielding, the means of introducing gases, and the variables involved with handling gases.

1.2 *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 safety, health, and healthenvironmental practices and determine the applicability of regulatory limitations prior to use.*

1.3 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

E416 Practice for Planning and Safe Operation of a Spectrochemical Laboratory (Withdrawn 2005)[3]

3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminology E135.

4. Significance and Use

4.1 An increasing number of opticalatomic emission spectrometers are equipped with enclosed excitation stands and plasmas which call for atmospheres other than ambient air. This practice is intended for users of such equipment.

5. Reference to this Practice in ASTM Standards

5.1 The inclusion of the following paragraph, or suitable equivalent, in any ASTM spectrochemical method, preferably in the section on excitation, shall constitute due notification that this practice shall be followed:

X.1 *Gas Handling*—Store and introduce the gas in accordance withas directed in Practice E406.

6. Concepts of Excitation Shielding

6.1 *Control of Excitation Reactions:*

6.1.1 Nonequilibrium reactions involving variable oxidation rates and temperature gradients in the analytical gap produce spurious analytical results. The use of artificial gas mixtures can provide more positive control of excitation reactions than is possible in air, although air alone is advantageous in some instances.

6.1.2 Methods of introducing the gas require special consideration. Temperature gradients in both the specimen and the excitation column can be controlled by the cooling effect of the gas flow. Also, current density can be increased by constricting the excitation column with a flow of gas.

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[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.

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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.

6.1.3 Control of oxidation reactions is possible by employing nonreactive or reducing atmospheres. For example, argon can be used to preclude oxidation reactions during excitation. A gas may be selected for a particular reaction, such as nitrogen to produce cyanogen bands as a measure of the carbon content of a specimen. Oxygen is used in some instances to ensure complete oxidation or specimen consumption. In point-to-plane spark analysis, a reducing atmosphere can be provided by the use of carbon or graphite counter electrodes in combination with an inert gas[3] or by the use of special circuit parameters[4] in ambient air.

6.2 *Effects of Controlled Atmospheres:*

6.2.1 Numerous analytical advantages can be realized with controlled atmospheres:

6.2.1.1 The elimination of oxidation during point-to-plane spark excitation can significantly reduce the so-called "matrix" effects and compositional differences. This can result in improved precision and accuracy.

6.2.1.2 The use of argon or nitrogen atmospheres in point-to-plane procedures can *increase* instrument response so that a wide range of ~~concentrations~~compositions can be covered with one set of excitation parameters, but because of the increased background, *small losses* in the detection limit can result from oscillatory high voltage spark excitation. Which effect occurs depends on wavelengths used.

6.2.1.3 Various forms of the Stallwood jet[5] are used in ~~d-c arc~~DC Arc-AES procedures. One gas or a mixture of gases can be used with this device depending on the particular analytical problem. Mixtures of 70 % argon and 30 % oxygen, or 80 % argon and 20 % oxygen are ~~routinely~~ used to eliminate cyanogen bands, reduce background intensity, and promote more favorable volatilization. Certain gases enhance intensity at various wavelengths.[6] The precision and accuracy achieved for most elements with ~~d-c arc~~DC Arc-AES procedures employing controlled atmospheres are significantly better than when ambient air is used. Such improvement is of particular value in trace analysis.

6.2.1.4 Self-absorption of analytical lines can be reduced by employing a suitable gas flow around or across the excitation column;[5] the flow of gas sweeps away the cooler clouds of excited vapor which cause the self-absorption. In argon, the diffusion of ions out of the excitation column is comparatively slow, and this also decreases self-absorption.

7. Means of Introducing Atmospheres

7.1 *Design Considerations*—Design of a device for excitation shielding involves the following: (*1*) degree of shielding needed, (*2*) type of excitation to be employed, (*3*) speed of specimen handling, (*4*) constructional simplicity, and (*5*) cost.

7.2 The purpose of the shield dictates its complexity; a totally enclosed system would be superfluous when a simple jet would suffice. The excitation employed dictates the choice of materials. With spark excitation, a plastic shield can frequently be used, but a more refractory material, such as alumina or heat-resistant glass, is usually necessary when employing an arc. Speed and ease of specimen handling are important design considerations for routine operation. Construction should be simple, employing easily obtainable materials and as few parts as possible. Provision should be made for conveniently cleaning the interior.

7.3 *Enclosed Chambers and Other Devices*—The method of introducing the atmosphere is determined by the intended purpose. For example, a totally enclosed chamber is necessary for excitation at all pressures other than atmospheric.

7.3.1 Shielding devices for point-to-plane spark analysis range from simple jets to more sophisticated dual flow designs. Frequently, these same devices are also suitable for use with arc excitation provided they can withstand the associated high temperatures.

7.3.2 Effective shielding for point-to-plane spark analysis in conventional excitation stands can be accomplished by the use of a chamber around the counter electrode. The gas is directed into the chamber and its outward flow envelops the counter electrode, analytical gap, and excited area of the specimen. Several variations of such a device are commercially available.

7.3.3 ~~Optical and excitation shielding is necessary with vacuum emission instruments for spectra below 2000 Å. Air is opaque to radiation in this region and must be replaced, for example, by argon,~~ Oxygen in air absorbs UV radiation below about 200 nm, therefore it must be replaced by either nitrogen or argon in order to permit transmission of ~~these wavelengths. Commercial vacuum spectrometers are equipped with gas-shielded excitation stands.~~ spectra in this wavelength region. Commercial AAS, ICP-AES, DCP-AES, GD-AES, and SparkAES instruments are available with vacuum specifications or either argon or nitrogen purged systems. In these instruments, a flat specimen ~~often~~ is often used to seal the excitation chamber. Other shapes can be accommodated if a special holder is constructed ~~to~~that also ~~seal~~seals the chamber. Such holders are commercially available.[7]

8. Variables Concerned with Gas Handling

8.1 *Gas Purity*—Gases used in excitation shielding must be of consistent purity. While total impurities as high as 50 ~~ppm~~µg/g may not affect analytical results when nitrogen is used, most suppliers can furnish inert gases with total impurity levels of 30 ~~ppm~~µg/g or less.

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[3] Schreiber, T. P., and Majkowaki, R. F.,"Effect of Oxygen on Spark Excitation and Spectral Character," *Spectrochimica Acta*, Vol 15, 1959, p. 991.

[4] Bartel, R., and Goldblatt, A., "The Direct Reading Spectrometric Analysis of Alloy Cast Iron," *Spectrochimica Acta*, Vol 9, 1957, p. 227.

[5] Stallwood, B. J., "Air-Cooled Electrodes for the Spectrochemical Analysis of Powders," *Journal of the Optical Society of America*, Vol 44, No. 171, 1954.

[6] Baker, M. R., Adelstein, S. J., and Vallee, B. L., "Physical Basis of Line Enhancement in Argon and Krypton," *Journal of the Optical Society of America*, Vol 46, 1956, pp. 138–140.

[7] Available from Thermo Jarrell Ash, 8 E. Forge Pkwy, Franklin, MA 02038.