



Designation: E 406 – 81 (Reapproved 2003)

Standard Practice for Using Controlled Atmospheres in Spectrochemical Analysis¹

This standard is issued under the fixed designation E 406; 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 optical 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²

E 416 Practice for Planning and Safe Operation of a Spectrochemical Laboratory³

3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminology E 135.

4. Significance and Use

4.1 An increasing number of optical 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:

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 *Annual Book of ASTM Standards*, Vol 03.05.

³ *Annual Book of ASTM Standards*, Vol 03.06.

X.1 *Gas Handling*—Store and introduce the gas in accordance with Practice E 406.

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.

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 gas⁴ or by the use of special circuit parameters⁵ 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 can be covered with one set of

⁴ Schreiber, T. P., and Majkowaki, R. F., “Effect of Oxygen on Spark Excitation and Spectral Character,” *Spectrochimica Acta*, Vol 15, 1959, p. 991.

⁵ Bartel, R., and Goldblatt, A., “The Direct Reading Spectrometric Analysis of Alloy Cast Iron,” *Spectrochimica Acta*, Vol 9, 1957, p. 227.

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 jet⁶ are used in d-c arc 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.⁷ The precision and accuracy achieved for most elements with d-c arc 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;⁶ 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.⁸

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.⁸

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.⁸

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, to permit transmission of these wavelengths. Commercial vacuum spectrometers are equipped with gas-shielded excitation stands. In these instruments, a flat specimen often is used to seal the excitation chamber. Other shapes can be accommodated if a special holder is constructed to also seal the chamber. Such holders are commercially available.⁹

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 may not affect analytical results when nitrogen is used, most suppliers can furnish inert gases with total impurity levels of 30 ppm or less.

8.1.1 Gases that have been packaged by means of water or oil-lubricated compressors are to be avoided because of possible contamination by moisture, organic species, or both. Industry practice is to produce and store the major inert gases, for example, argon and nitrogen, in liquid form. In general, the terms “water pumped” and “oil pumped” are only classifications and do not relate to the types of compressor lubrication. The major inert gases are usually packaged directly from the liquid phase through impeller pumps and head exchangers. However, helium is not liquefied and is packaged under pressure immediately after purification. Additional pressure, if needed, is furnished by nonlubricated diaphragm pumps. Some small producers using gaseous liquefaction plants still employ oil or water compressors for packaging under pressure. Therefore, conditions of manufacture and purity must be evaluated locally in light of the laboratory requirements.

8.1.2 Those instruments with enclosed gas-shielded excitation stands usually employ a pointed counter electrode of thoriated tungsten, copper, silver, or other metal. Because the excitations used usually are polarized oscillating sparks where the current does not pass through zero, additional purification of even the liquid argon may be necessary to achieve the proper sampling. The purification can be accomplished by passing the gas through a reducing atmosphere furnace, containing titanium, at 427°C (800°F) to remove oxygen and moisture, or other purification such as molecular sieves may be used. In addition, ample exit ports for the gas must be provided to remove debris. For each enclosed excitation stand, there exists a critical flow rate and pressure. These must be determined in order to achieve proper sampling and excitation.

NOTE 1—Some specimens are inherently difficult to excite; for example, NBS Ductile Irons Nos. 1142 and 1142a, and NBS Leaded Steel No. 1169. Some users have found that even with apparently good specimens, one in fifty burns might be bad (superficial) for no obvious reason. A superficial burn produces a whitish film on the surface of the specimen and the intensities obtained for the analytical and internal

⁶ Stallwood, B. J., “Air-Cooled Electrodes for the Spectrochemical Analysis of Powders,” *Journal of the Optical Society of America* Vol 44, No. 171, 1954.

⁷ 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.

⁸ Available from both Spex Industries, Inc., 3880 Park Ave., Edison, NJ 08820, and Angstrom, Inc., Box 248, Belleville, MI 48111.

⁹ Available from Thermo Jarrell Ash, 8 E. Forge Parkway, Franklin, MA 02038.