Designation: E 406 – 81 (Reapproved 2003)

# Standard Practice for Using Controlled Atmospheres in Spectrochemical Analysis[1]

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 Materials[2]

E 416 Practice for Planning and Safe Operation of a Spectrochemical Laboratory[3]

## 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:

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 gas[4] or by the use of special circuit parameters[5] 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

[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.

[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 jet[6] 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.

standard lines are generally inadequate. For some instruments, this may also result in a long integration time.

8.2 *Packaging and Storage*:

8.2.1 High-pressure gas cylinders are more common, but liquid-state containers are also used. Depending on the gas, high-pressure welding-size cylinders, when full, will contain from 15 to 18 MPa (2200 to 2650 psi). Widespread availability and long storage life favor the use of the high-pressure cylinders. However, they are relatively inefficient and deliver only 5700 to 6500 L (200 to 230 $ft^3$) of gas per cylinder so that the space and handling considerations may be important. Although only slightly larger than the high-pressure cylinder, a standard 30-gal liquid container will deliver 10 to 14 times the volume of gas. For example, 1 gal of liquid nitrogen is equivalent to 2630 L (93 $ft^3$) at 20°C and atmospheric pressure; thus, a 30-gal container will deliver 2630 L × 30 or 97 000 L (2790 $ft^3$) of nitrogen gas.

8.2.2 Liquid gas containers cannot be stored for extended periods because of the necessity for venting. Due to heat losses through the container, equilibrium conditions are not possible between the liquid and gaseous phases; consequently, the container continuously exhausts excess pressure so that significant amounts of gas are lost over long periods.

8.2.2.1 Installation of liquid gas cylinders so that they stand on a scale to monitor their weight and where they can be connected with purge lines to permanent copper tubing leading to the spectrometer is desirable. One instrument manufacturer recommends a scale capacity of 453 kg (1000 lb). The liquid containers should be returned with a minimum of 11 kg (25 lb) above tare weight, and the high-pressure cylinders should be returned with a minimum of 172 kPa (25 psi).

8.2.3 If high purity is necessary, liquid containers offer the greatest degree of consistency. Such containers are recommended particularly when unidirectional condensed discharges are used, because impurities in the gas suppress the "energetic-type burn." High-voltage spark discharges using graphite counter electrodes are not, in general, as dependent on gas purity.

8.2.3.1 It is strongly recommended that an arrangement be made with the gas supplier whereby the user will have the exclusive use of certain tanks. Either by recording the serial numbers or using a distinctive mark, the same tanks can always be identified and set aside for the user.

8.3 *Flow System*—A basic gas flow system for excitation shielding contains the following components: (*1*) a two-stage regulator with pressure gages, (*2*) a flow-metering valve, (*3*) a flow indicator, and (*4*) tubing for gas transport. The basic function of the system is to deliver to the shielding device a constant flow of gas at a given pressure.

8.3.1 Incorporating a dual-stage regulator provides pressure reduction and simultaneous monitoring of the cylinder pressure and the outlet pressure. The outlet pressure should be maintained at a definite level since this determines the pressure at the shielding device.

8.3.1.1 Dual-stage regulators are commercially available; but, care must be exercised to obtain the proper type for the gas to be used. Adapters are available that will allow the use of one regulator with several different gases; however, this practice presents serious safety hazards and danger of cross-contamination. Some regulators introduce significant amounts of impurities through leakage and degassing. Special regulators are available for handling high-purity gases. Because of aging and adsorption, metal diaphragms are preferred over rubber ones.

8.3.2 The metering valve controls the flow of the gas and should be precise in operation and sized to handle the intended flow rate. Frequently, it is incorporated in the flowmeter to provide an integral unit capable of controlling and indicating flow rates. Flowmeters may be calibrated for specific gases, or they may be of the universal type with separate calibration curves for different gases.

8.3.3 Tubing materials of metal or plastic with low-moisture and gas-retention properties are preferred. For example, both copper and thick-walled TFE-fluorocarbon are satisfactory, although copper is preferred; rubber and plastics, other than TFE-fluorocarbon, are to be avoided because they absorb moisture and gases.

8.4 *Filtering*—Most enclosed excitation stands have a filter mechanism to remove the elemental particles entrained in the gas which are products of the vaporization of the specimen. The particles are very small and can be a source of spontaneous combustion if not disposed of safely. Some manufacturers recommend routing the spent gas through a water bath and thence to the atmosphere. Others recommend collecting the fine particles in a filter medium and disposing of them under water. The material should not be emptied into wastebaskets. Filters should be changed when necessary to maintain correct desired excitation conditions. It is strongly suggested the spent gas be exhausted outside the laboratory.

## 9. Safety Hazards

9.1 It is not in the province of this practice to itemize all safety precautions for all pressurized or liquid gases, or both. Laboratories using such gases should consult safety practices of their own safety departments as well as consult those of the gas suppliers. Limited precautions are found in Practice E 416.

## 10. Keywords

10.1 controlled atmospheres; spectrochemical analysis