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By Dr. Monte J. Solazzi

Disposable sample cups for X-ray fluorescence analysis

TECHNOLOGICAL advancements in both wavelength-dispersive (WDXRF) and energy-dispersive (EDXRF) x-ray fluorescence instrumentation have given the spectroscopist the means to accommodate virtually all types of sample materials. Higher degrees of analytical accuracy and precision and lower limits of detection and concentration levels can be achieved. As a result, refinements in sample presentation methods have been made and, in many instances, new systems and adjunct equipment have been introduced. Sample analysis times decreased dramatically, and x-ray fluorescence is now recognized as a versatile laboratory tool useful for both infrequent and routine sample analysis.

Sample preparation is frequently more time-consuming than the actual analysis. This is particularly true with powdered solid sample materials as a result of the need to reduce sample particle size differences and inhomogeneities to insignificant levels. Solution samples, in most cases, simply require transfer to an appropriate device for containment and presentation to the instrument. Unlike powdered solid or solid samples, the constituent elements in solution samples are assumed to be in complete states of dissolution: as long as the laws governing critical depths of penetration are observed, no further processing is usually required.

This paper describes a line of disposable plastic XRF sample cups (Chemplex® Industries, Inc.) for use with powdered solid, liquid, and solid sample retention. The cups are used to present samples for x-ray fluorescence analysis, and contribute to efficiency in sample handling methods and diversification of applications.

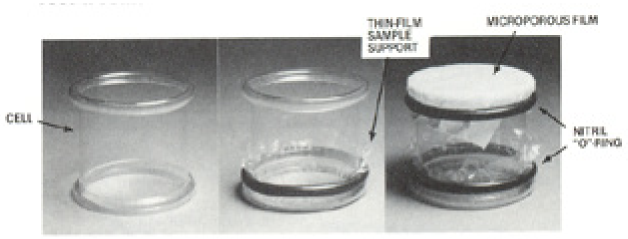


FIGURE 1A FIGURE 1B FIGURE 1C

Figure 1 *Dispoza-Cups.*

Product Development

The first Chemplex disposable x-ray fluorescence sample cups were called Dispoza-Cups. The body, or cell, of the cup shown in Figure 1a, was fabricated of tubular cellulose acetate butyrate cut into appropriate lengths to fit into metallic sample holders on the instrumentation. The ends of the cell were thermo mechanically turned down and under to form smooth, rounded beads to which thin-film sample supports with nitrile O-rings were affixed (Figure 1b). A conically shaped aluminum device was designed to stretch the nitrile “O”-ring as it was guided to roll over the beaded edge of the cell to effect a seal.

Dispoza-Cups were useful in eliminating time consuming and costly clean-up operations, and for reducing the possibility of cross contamination. Their use and applications were mainly in the oil and petrochemical industries. Significant drawbacks prohibited their use in effectively retaining the types of sample materials normally conducive to x-ray fluorescence analysis. The cellulose acetate butyrate material did not offer adequate resistance to chemical attack and degradation or softening from intense energy source excitation. Also, since the cell end obverse to the thin-film sample support was open, analyses of many types of sample materials were limited to applications in air or inert gas environments. To resolve the difficulties associated with pressure inequalities, a gas-permeable, chemically unreactive polypropylene membrane, called microporous film, was used as a cover for the open end of the Dispoza-Cup, and was attached similar to a thin-film sample support with a nitrile “O”-ring (Figure 1c).

Microporous film is characterized by 0.1mm channels (35% porosity) that permit the permeation of gaseous-size molecules, while at the same time prohibiting the penetration and withdrawal material from the cell. Microporous film maintains continuous equalization of pressure within the sample cup and sample chamber, thereby averting potential distention or retraction of the thin-film sample support and subsequent alteration of the sample-to-excitation source distance. The use of other plastic materials was then investigated, and a complete cell design change was made that incorporated a type of clamping ring to firmly and easily secure a thin-film sample support. Injection molding was found to be the best method for manufacturing sample cups in volume, a procedure that was adaptable to a large variety of thermoplastic materials.

Fifteen different disposable XRF sample cups are currently available for use with a wide range of commercial x-ray spectrochemical analyzers. The cups are made of polyethylene, which is resistant to chemical degradation, deterioration by excitation of source exposure, and thermal softening by x-ray bombardment. Polyethylenes also resists thin-film distortion during and after assembly, is elastic or ease in firmly securing thin-film sample supports without formation of pinholes, and is pure, particularly with regard to sulfur content.

Thin-Film Sample Support Attachment

The design of the cell neck on Chemplex XRF sample cups, in conjunction with the snap-on ring, retains the thin-film sample support in position and maintains it continuously taut up to the completion of assembly. Figure 2 shows the mechanism responsible for effective thin-film sample support preparations. One end of the snap-on ring (Figure 2a) has a semi-spherically shaped "bead" around the interior circumference. Below the bead, the diameter decreases toward the opposite end to form a taper on the inside of the snap-on ring. The cell neck (Figure 2b) has a similar taper on the outer diameter that increases beginning from the edge and extending toward a semispherical indentation around the circumference. The inside diameter of the bead is slightly larger than the outside diameter of the cell neck at the edge. Extending a small distance from the cell neck edge, the bead of the ring meets resistance to further assembly from the increasing cell neck taper. Thus the thin-film sample support material is initially grasped and held taut at all points of contact by the bead and is temporarily stretched (illustrating the need for thermoplastic elasticity) until the bead finally locks into the cell neck (Figure 2c). The thin film sample support thus formed is leak-resistant, wrinkle-free, and taut, reducing the chance of contamination.

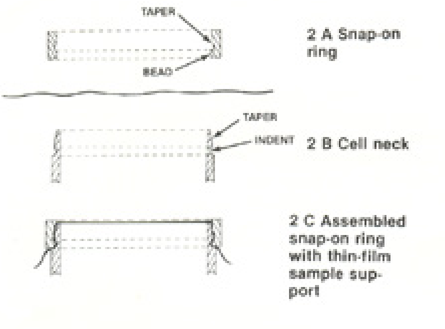


Figure 2 *Cross-sectional illustration of snap-on ring and cell neck configurations.*

The distances from the cell neck edge to the indentation, and from the bead to the opposite end, are slightly dissimilar; the ring extends a slight distance beyond the cell neck. The difference in length prevents the sample support from contacting the surface preparation area and introducing contamination or accidental puncturing. **In** addition, the snap-on ring will not fit the cell neck unless positioned properly.

Open cell 1500 XRF sample cups

The 1500 Series XRF sample cups, the successors to the Dispoza-Cup, consist of a cell open at both ends and two identical snap-on rings (Figure 3). The ends of the cell incorporate tapered and beaded snap-on rings for attachment of thin-film sample supports, microporous film, and the 1600 Series sample cup caps. A ridge at the outer circumference adjacent to the indentation at one end of the, cell shows which is the appropriate side for installing microporous film. As a general rule, microporous film and sample cup caps are attached to the ridged end of the cell, and thin-film sample supports are secured to the opposite end.

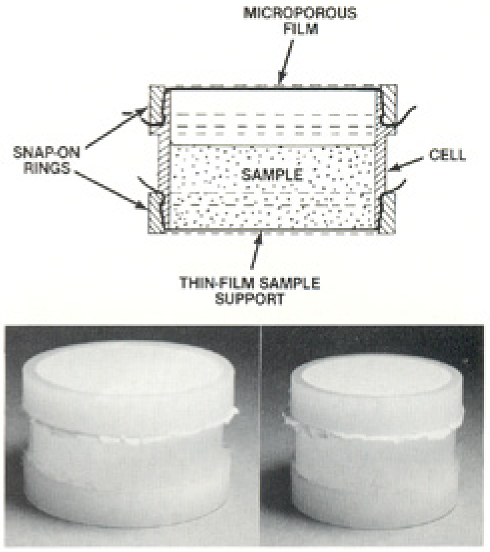


Figure 3 *Diagram and photograph of open-cell sample cups.*

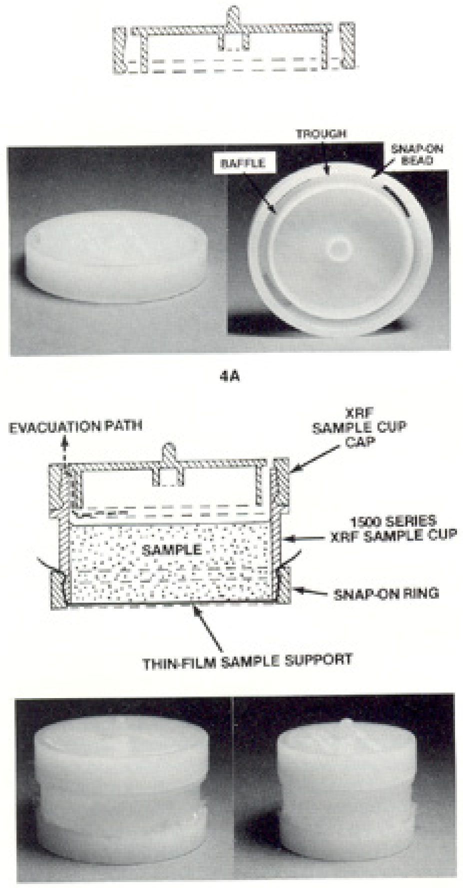
A thin-film sample support is positioned over the cell, and a snap-on ring is placed on it and pushed downward to complete assembly, as indicated by a clicking sound. The cell is inverted and a sample is introduced through the top open end and presented for analysis. To avoid spillage during handling or analysis, the open top end of the cell is covered using either microporous film with a second snap-on ring or a 1600 Series sample cup cap. Some analysts reported use of a thin-film sample support on the open top end, but this is not recommended because of significant pressure differentials that may affect the excitation source-to-sample distance or cause a thin-film rupture.

The 1500 Series cups are available in 32 mm (12 ml sample capacity) and 40 mm (18 ml capacity) diameters, 23 mm in height. The aperture (inside diameter of the cell measured at the opening) is 25 mm and 32 mm respectively for the two sizes. Translated into sample surface areas available for analysis, the 32 mm cups provide 493 mm^2 and the 40 mm cups 807 mm^2.

Sample Cup Caps

The 1600 Series XRF sample cup caps are used with the open cell sample cups. The caps maintain continuous equalization of pressure between the sample cup and sample chamber concurrent with sample containment.

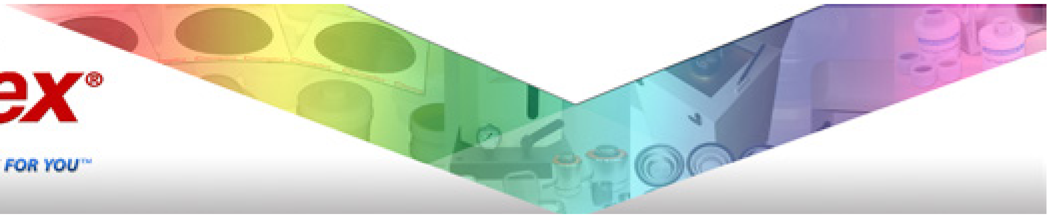
Sample cup caps, when assembled to a 1500 Series sample cup (Figure 4), are designed to keep a specimen from escaping. The underside of the cap contains a trough between a circular baffle adjacent to an outer circumferential ring. The inside surface of the outermost ring has a semi spherically shaped bead that mates with the indentation in the cell neck. The flat plane of the sample cup cap contains four narrow slits that coincide with the circular narrow trough. When the cap and cup are assembled, the cell neck positions itself in the trough, leaving a narrow passageway to the slits for pressure equalization. The winding passageway prevents material from escaping.



4A

4B

Figure 4 *Diagram of XRF sample cup cap.*



Closed Cell Sample Cups

The 1400 Series closed cell XRF sample cups* (Figure 5) are thermo plastically sealed at one end during the injection molding process and incorporate special features that enhance their versatility.

As with all Chemplex XRF sample cups, the design for the closed-cell cups includes the thin-film sample support "clamping" method for attachment. The closed outside end contains two small circular depressions that are for vent-holes for pressure equalization purposes. One vent-hole is centrally located and the other is off-center. Both are sealed during the injection molding process and can be easily ruptured by a blunt instrument or an automatic vent-hole punch, supplied as an accessory, for establishing pressure equalization. For routine applications, the cell is filled with a sample material and a thin-film sample support is attached with a snap-on ring. The assembled cup containing the sample is inverted and the central vent-hole seal is punctured to establish pressure equalization in air, helium, or vacuum atmospheres.

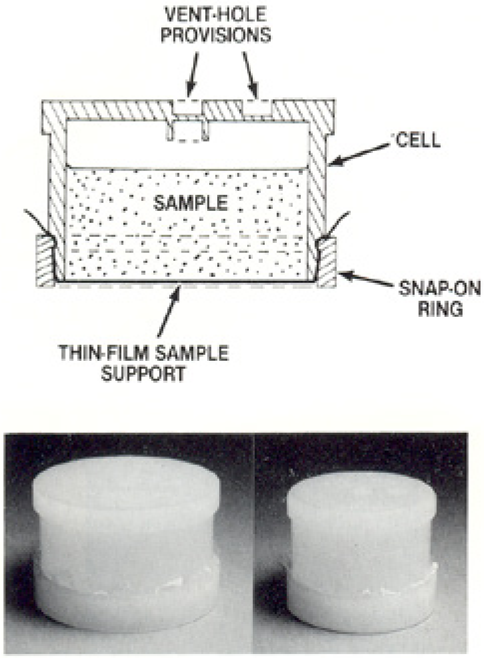


Figure 5 *Diagram of 1400 Series XRF sample cups.*

For special applications, the underside of the closed end contains a receptacle in the center directly opposite the exterior center vent-hole provision (Figure 6) for insertion of a capillary tube or rod to which a micro sample or internally positioned reference material may be attached. The inside diameter of the receptacle is 4 mm, and the receptacle is slightly tapered to accept and firmly retain a rod or capillary tube of similar outside diameter. Different lengths of rod or capillary tube can be used. The off-center vent-hole serves to equalize pressure in applications using the built-in central receptacle. The secondary function of the receptacle is to reduce sample escape during evacuation and to impede the flow of oil-type specimens, which tend to adhere and creep along a surface,

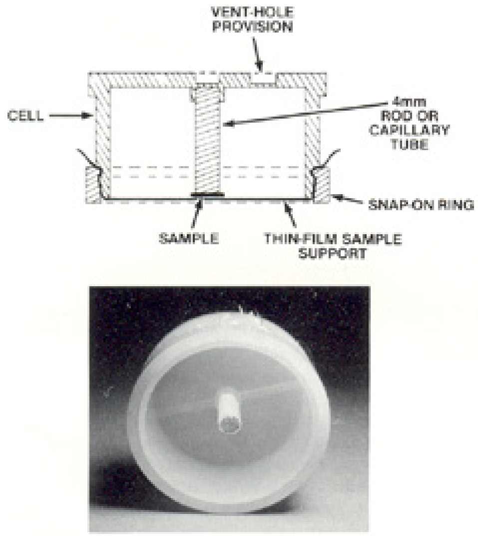


Figure 6 *Diagram of 1400 Series cup with microsample mounting feature.*

The 1400 Series cups have a collar that entraps or "sandwiches" powdered solid or evaporated liquid specimens between two pieces of thin film (Figure 7), The collar is first introduced to attach a thin-film substrate to the cell; the specimen is deposited on the substrate, and a second thin-film sample support is secured directly over this with a snap-on ring, thereby entrapping the specimen. A third piece of thin film is frequently used to uniformly spread or distribute sandwiched powdered solid sample, to encompass as much surface area as the quantity of specimen allows, The collar is also used to position a sample-impregnated filter paper prior to final assembly with a snap-on ring, Many users initially position a thin-film sample support with a collar prior to final assembly with a snap-on ring, as an added convenience. Closed cell cups are available in 32 and 40 mm diameters with volumetric capacities of 12 and 18 ml respectively, the sample exposure or excitation impingement area is 493 mm^2 for the 32-mm size and 807 mm^2 for the 40-mm version, both sizes are 23 mm in height.

Sample Cups for Heat-Sensitive Liquid Samples

The 1800 Series XRF sample cups (Figure 8) accommodate heat-sensitive liquid samples that tend to expand when subjected to intense irradiation or reduction in atmospheric environment. The top end of the closed cell has an overflow reservoir to collect and retain thermally expanded sample materials or oil specimens, which are characterized by their tendency to "creep," and which may escape through the punctured vent-hole, The 1800 Series sample cups have all of the features of the 1400 Series cups, with the exception of the interior receptacle for micros ample mounting, The cups have snap-on rings and collars for thin-layered sandwiched evaporated liquid or powdered solid sample preparations.

Two sizes are available: 32 mm and 40 mm diameters. The 32 mm size accommodates 7 ml of sample material, and the overflow reservoir accepts up to 3 ml. The 40 mm cup will contain 12 ml of sample, with an overflow reservoir of 5 ml. The 32 mm diameter cup exposes 493 mm^2 of sample surface area for analysis, and the 40 mm size exposes 807 mm^2. Both are 23 mm in height.

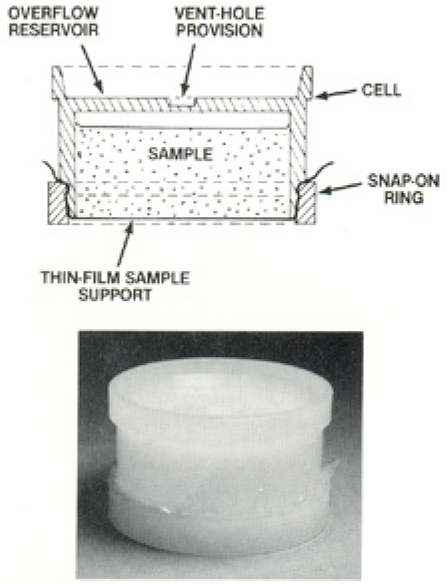


Figure 8 *Diagram of 1800 Series cup with overflow reservoir.*

Specially Designed Sample Cups

Requests from spectroscopist and x-ray fluorescence instrumentation manufacturers have led to the development of specially configured XRF sample cups, all incorporating the "clamping" method of thin-film sample support attachment.

The 1850 Series disposable, polyethylene XRF sample cup (Figure 9) is designed for use with Horiba SLFA Series instrumentation. The cup features a vent-hole for pressure equalization, an overflow reservoir of 6 ml capacity, and a cell that contains 15 ml of sample. The outside diameter of the 19-mm-high assembled unit is 47 mm. The aperture of the 1850 sample cup is considerably larger in diameter-36 mm-than other cups, and permits a sample exposure area of 1022 mm^2. This sample cup is not limited to use with Horiba instrumentation. Many analysts have found the large sample exposure area beneficial in decreasing the influence of powdered solid sample surface irregularity on x-ray data and in reducing integration time. The instrument, however, must be able to accept a sample at least 50 mm in diameter.

Instruments manufactured by Oxford Analytical require disposable sample cups 37 mm in length to accommodate the long depth of excitation source penetration and to avoid impingement with the sample cup. Two disposable sample cups were developed for Oxford Lab-X spectrometers. The 1440-L cup has a closed cell and the 1540-L is open on both sides, with one end containing a slight ridge for convenience of handling. The closed 1440-L cell has a vent-hole provision for pressure equalization. Both cups are 37 mm long and 40 mm in diameter, with volumetric capacities of 25 ml and a sample surface exposure area of 493 mm^2.

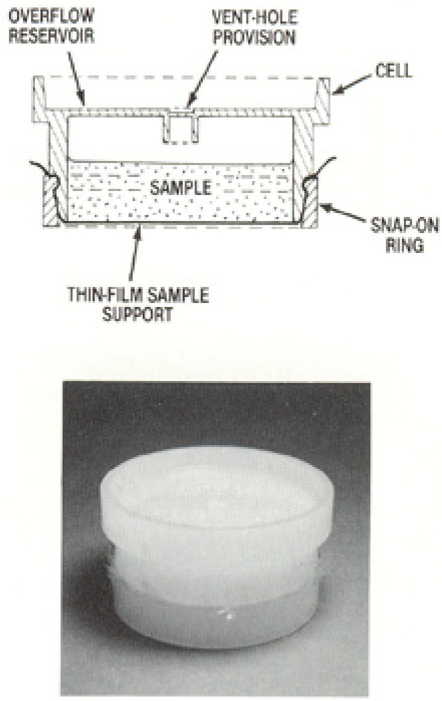


Figure 9 *Diagram of 1850 Series cup, 47 mm in diameter.*

Convertible Closed/Open cell Sample Cups**

Another unique sample cup design is a convertible closed/open cell (Figure 10). The cup consists of a snap-on ring for attaching a thin-film sample support, an open cell, and a leak-resistant snap-on cap for insertion into the upper open end, thereby converting the open cell to a closed version. The snap-on cap is secured to the cell by the bead and indentation design and can be rotated by force.

A small cutaway in the snap-on cap at the circumference corresponds to a vertical groove in the inside cell wall that extends a short distance to the upper surface. When these are fitted together, an unobstructed passageway from the interior of the cell is established for pressure equalization. Misalignment of the cutaway with the vertical groove converts the cell to a closed unit (Figure 10b).

In practice, the snap-on cap is first inserted in place in a sealed position. The cell is inverted and a liquid or powdered solid sample is introduced, followed by attachment of a thin-film sample support. Prior to analysis, the cap is rotated to the appropriate position for pressure equalization. An overflow reservoir built into the snap-on cap collects heat sensitive liquid samples that may expand as a result of heat generated by intense excitation; This XRF sample cup style is available in 32 mm and 40 mm diameter sizes, both 23 mm in height. The 32 mm cup exposes 493 mm^2 of sample area, and the 40 mm version exposes 807 mm^2.

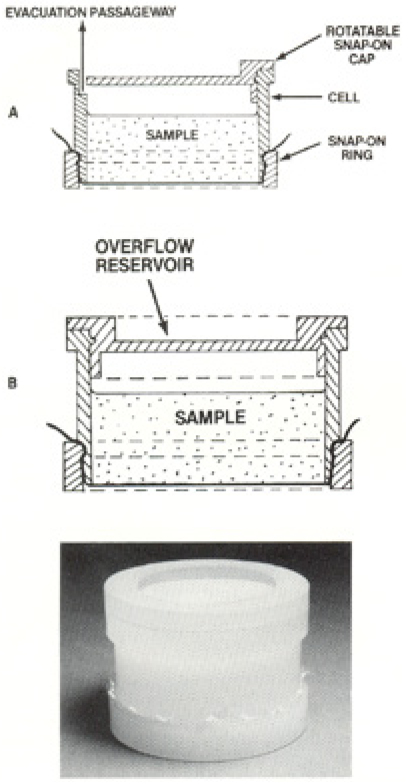


Figure 10 *Diagram of convertible closed-open cell cups.*

Push-Plunger ***, Self-Venting XRF Sample Cups

A disposable XRF sample cup similar to the 1400 Series features a grooved plunger attached in the center to the closed end of the cell (Figure 11). The plunger punctures the thermoplastic seal to equalize pressure within the sample cup and its external environment. This cup features an overflow reservoir; other specifications are similar to those for the 1400 Series cups, including availability of both 32 mm and 40 mm diameter sizes.

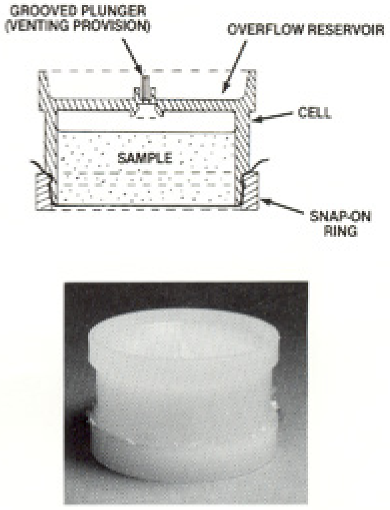


Figure 11 *Diagram of push-plunger XRF sample cup.*

Thin-Film Sample Supports

As the range of elemental detect ability to lower atomic numbers and concentrations has been extended, the need for thin-film sample supports characterized by greater analyte-line transmittance properties and greater sample retention strength has also increased. Polyethyleneterephthalate (Mylar®), available in 6.3, 3.6, and 2.5 μm gauges, together with 6.3 μm XRF polypropylene film and 7.5 μm polyimide (Kapton) thin-films, give analysts a range of sample supports for a variety of needs. Figure 12 shows the relative percent transmittance for each thin-film sample support material and gauge to analyte-line wavelength up to 14 Angstroms.

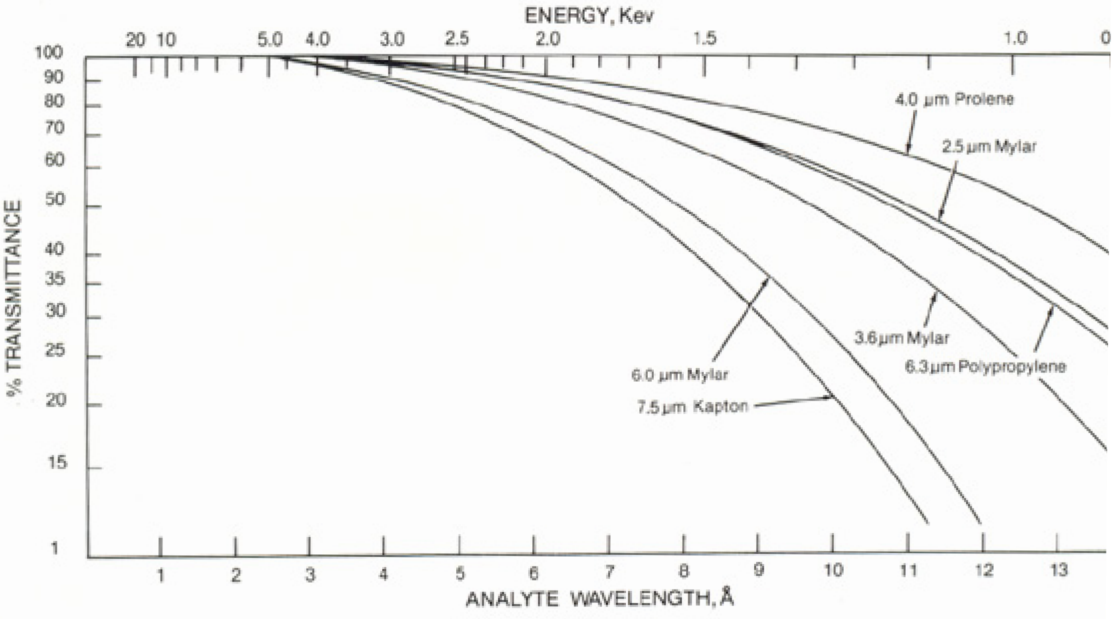


Figure 12 *Relative percent transmittance and gauge for thin-film sample support material*

Summary

A broad range of disposable XRF sample cups have been described that were developed in response to advances in WDXRF and EDXRF instrumentation. The cups aid in sample handling and increase efficiency. The cups feature a unique tapered snap on ring with a bead and indentation assembly that clamps the thin-film sample support. Supports come in a variety of materials and gauges.

XRF sample cups are manufactured in the United States in a range of styles, sizes, and specialized features, and can be shipped on the day of order. Engineering expertise, tooling, and supporting equipment are available at the manufacturer to accommodate the special needs of instrumentation manufacturers and users for quality XRF sampling accessories.

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Dispoza-Cup is a trademark of Chemplex Industries, Inc.
* Registered US Patent Number 238,693
** Registered US Patent Number 4,698,210
*** Registered US Patent Number 4,409,854

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X-ray fluorescence thin-film sample support materials

Figure 1.
Thin-Film Sample Support Materials

THE RETENTION of liquid, powdered solid, solid, and slurry samples in disposable XRF Sample Cups (Chemplex® Industries, Inc.) in preparation for energy- (EDXRF) and wavelength-dispersive (WDXRF) x-ray fluorescence (XRF) spectrochemical analysis has been previously described [1]. This report describes the various types of sample cups available, some advancement in thin-film materials and the parameters used to assess them, and illustrates the influence of these materials on analyte-line transmittance.

Since the inception of WDXRF and EDXRF instrumentation, rapid technological developments have extended the range of analytical interest to lower atomic number elements, lower limits of detection, and diversified scientific disciplines, thus necessitating thin-film sample support materials more reproducible in gauge thickness and providing higher analyte-line transmittance.

A substance used in thin-film sample supports must exhibit a relatively high degree of resistance to chemical attack, excitation energy source, embrittlement or degradation, thermal softening, and deterioration from the heat generated by excitation exposure, and possess relatively good sample retention strength. The materials must also be reasonably free of impurities and possess the necessary combination of chemical composition, density, and gauge to impart minimum absorption of both the primary (excitation energy) and secondary (analyte-line) radiation.

Until 1972, the most commonly used thin-film sample support material was 6.3 μm gauge polyethylene terephthalate (Mylar®). Later, 2.5μm and 3.8 μm gauges were introduced. These three gauges together effectively accommodated virtually all areas of analytical interest, but due to a change in the manufacturing process of Mylar, trace quantities of Ca, P, Sb, and Zn were detected. Converting to a different grade of Mylar reduced the concentration of these elements, and two of the gauges were substituted with 3.6 and 6.1 μm gauges. In addition, three polymeric materials-polypropylene, polyimide, and polyethylene-qualified as thin-film sample supports and were found to be relatively free of potentially interfering impurities.

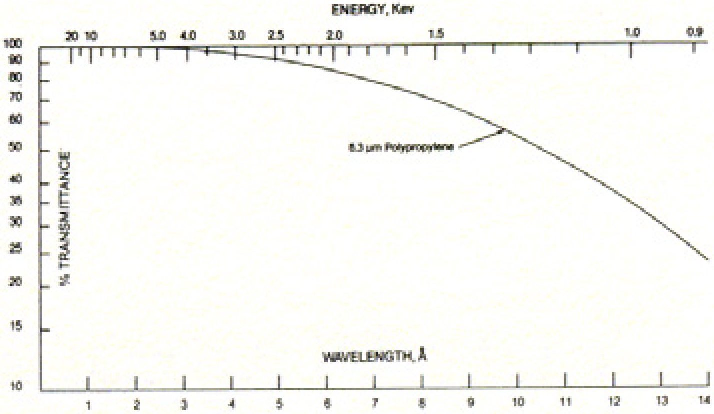

Figure 2 *Analyte-line correlation to percent transmittance.*

Initially, a suitable polypropylene was difficult to locate since a specific biaxially oriented type was required to avoid stretching. Thin-film supports must resist stretching and subsequent random alteration of gauge thickness and variations in analyte-line transmittance. X-ray polypropylene (Chemplex Industries, Inc.) was later offered in a 6.3 μm gauge as a replacement for Mylar. Although 6.3 μm gauge polypropylene resulted in a 5.4% decrease in analyte-line percent transmittance in comparison to the 2.5 μm gauge Mylar at 12.4 Angstroms, only a slight increase in integration time was required. Polyimide (Kapton®) in 7.6 μm gauge was also offered for specialized applications requiring increased sample retention strength for the more active analyte-line investigations and for vacuum applications. These thin-film sample support materials are shown in Figure 1.

The suitability of a substance for use in thin-film sample supports depends on its ability to permit analyte-line transmittance. This property is determined from the total mass attenuation coefficient of the material in combination with its area concentration for a given analyte-line, obeying Lambert's law in accordance with the following formula:

$$I = I_o \exp [- (\mu/d)\, dt]$$

Where, I = incident intensity;
I_0 = transmitted intensity;
μ/d = mass attenuation coefficient, cm^2/g
dt = area concentration, g/cm^2

This relationship shows the dependence of analyte-line transmittance on thin-film chemical composition, density, and thickness: $(\mu/d)(dt)$. Since the total mass attenuation coefficient of a thin-film material for a specific analyte line is based on the sum of its elemental constituent values, the chemical composition of the substance is critical and determines suitability for this application.

Rearrangement of the equation to express the percentage of incident and transmitted radiation, I/Io, as a function of mass attenuation coefficient, density, and thickness, exp $[-\{\mu/d)(dt)]$, provides a visual presentation of analyte-line transmittance through the thin-film substance.

Figure 2 demonstrates the reduction in percent transmittance with increased analyte-line wavelength (decreased keV values) for 6.3 μm gauge polypropylene. The effect of thin-film thickness on analyte-line transmittance is illustrated in Figure 3. The curves represent the percent analyte-line transmittance relationship for the same thin-film substance. (Mylar was arbitrarily chosen as the test material.) The displacement of the curves from one another is attributed to gauge differences. Note that absorption effects predominate in the long wavelength (low keV) region; the more energetic analyte lines tend to penetrate a thin-film substance with very little resistance as transmittance approaches 100%.

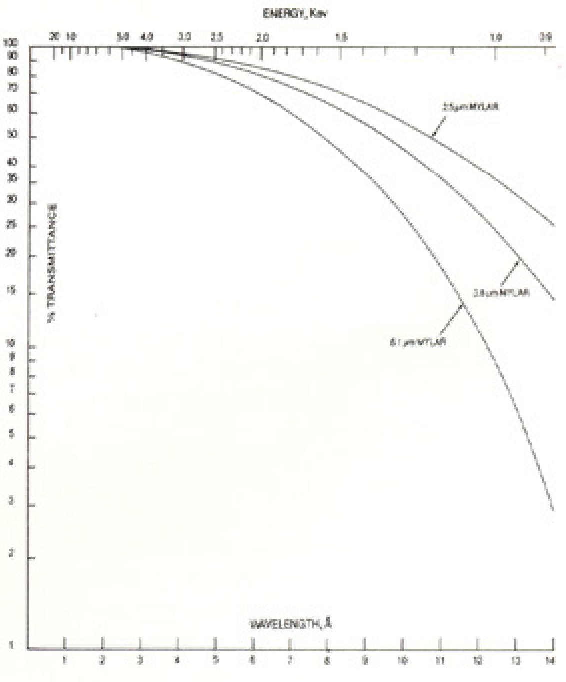

Figure 3 *Analyte-line transmittance as a function of substance and gauge.*

Other thin-film substances and gauges have been similarly assessed. The resultant curves differ completely from one another in individual combinations of mass attenuation coefficient, density, and gauge relationships. By constructing a series of superimposed curves encompassing a variety of thin-film substances and gauges, a rapid and effective visual means is established for selecting the most applicable thin-film material and thickness for specific analyte investigations (see Figure 4). However, other influential variables-the properties more directly associated with sample retention-are equally significant to thin-film material and gauge selection.

Degradation Resistance

A thin-film substance is also assessed by properties jointly classified as "degradation resistance." Degradation resistance as defined here represents the ability of a thin-film material to safely retain a specimen in an XRF sample cup during preparation and analysis. Degradation resistance includes resistance to chemical attack, thermal softening, embrittlement, tearing, and stretching.

The immediate chemical attack on a thin-film substance by contact with a specimen is usually obvious. However, deterioration is not always so evident: it may worsen with time or by heat induced from excitation, embrittlement from excitation energy exposure, or a combination of these and other events.

Although it is important to use the thinnest possible gauge thin-film substance to maximize analyte-line transmittance, very thin gauges tend to increase the threat of rupture under the weight of the specimen or under pressure differential created when the sample being analyzed is contained in a sealed sample cup in vacuum. A substance characterized by relatively high tensile strength is required. The tensile strength associated with most polymeric substances described is almost equal to 5000 psi. The thickness of the film then becomes the principal governing factor for sample retention strength.

A thin-film material must also resist stretching. Any changes associated with the thickness of a thin-film material are reflected by the degree of analyte-line transmittance and its influence on analytical accuracy. Any stretching of a thin-film material upon attachment to a sample cup will be reflected in the analytical data. Under vacuum, a differential in pressure between a sealed sample cup and the optics will cause the thin film to distend, creating two problems: a decrease in the distance from the excitation source to sample plane (defined by the thin-film sample support surface plane), resulting in false higher intensity measurements and analyte concentrations, and a decrease in the thickness of the thin film by stretching, resulting in an increase in analyte-line transmittance, thus implying a higher analyte concentration than actually exists.

In assessing thin-film substances, little information was available relating analyte-line transmittance and degradation resistance properties. Chemical and physical characteristics are generally expressed in terms of tensile strength, elongation, tensile modulus, tear strength, type of substance related to diversified and extended time and temperature exposures-all of which leave interpretation and evaluation to the spectroscopist for thin-film sample support applications.

A substance-screening procedure for thin-film applications that assigns a rating value combining degradation resistance and analyte-line percent transmittance properties emerged based on two criteria: failure of a single critical property or a combination of less critical individual properties. Substances were classified as good, fair, or poor (Table 1) and were related to chemical classifications as a common denominator for ease of referral and comparison instead of the conventional chemical material listings traditionally provided in chemical classifications.

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Table 1
Degradation Resistance of Thin-Film Substances

Chemical Classification	Mylar®	Polycarbonate	Etnom®	Polypropylene	Polyimide (Kapton®)	Prolene®	Ultra-Polyester®
Acids, dilute or weak	G	G	G	E	N	G	G
Acids, concentrated	G	G	G	E	N	E	G
Alcohols, aliphatic	N	G	G	E	G	E	N
Aldehydes	U	F	F	E	E	E	U
Alkalis, concentrated	N	N	G	E	E	E	N
Esters	N	N	F	G	G	G	N
Ethers	F	N	F	N	U	N	F
Hydrocarbons, aliphatic	G	N	E	G	E	G	G
Hydrocarbons, aromatic	N	N	E	N	E	N	N
Hydrocarbons, halogenated	F	N	F	N	F	N	F
Ketones	N	N	G	G	G	G	N
Oxidizing Agents	F	N	F	F	N	F	F

E = Excellent, **G** = Good, **F** = Fair, **N** = Not Recommended, **U** = Unknown

NOTE: The information contained in the above illustrations is provided as a matter of information only and it is not intended to preclude actual testing of the subject material for suitability of use and applications.

Percent Transmittance Comparisons

Most polymeric materials permit 95% to 100% transmittance through all gauges for analyte lines less than 4 Angstroms (3.1 keV). With increasing analyte-line wavelength for a particular thin-film material, the need for a thinner gauge correspondingly increases because of higher degrees of absorption. In evaluating a thin-film substance, the entire range of analyte lines of interest and anticipated analyte concentrations in a specimen should be considered. Thin-film material and thickness should be selected that provide the greatest degree of transmittance, particularly for low concentration levels and long analyte-line wavelengths, together with other pertinent properties. In many instances, the analytes and concentration levels are not previously known and a general-purpose thin-film substance should be used.

Teflon prohibits 50% analyte-line transmittance at 3.1 keV and Kapton loses 50% of its analyte-line transmittance at 1.7 keV. Both substances are, however, very well-suited for use as thin-film sample supports because of their excellent degradation resistance, but are limited (Teflon in particular) to use with the more energetic analyte lines.

Mylar exhibits good properties with respect to degradation resistance and percent analyte-line transmittance, but it has the drawback of inherent detectable trace levels of impurities. This can be a problem if the same elements at similar concentrations are to be quantified.

A superficial examination of polycarbonate shows this substance to be acceptable for thin-film applications based on its analyte-line transmittance, which is very similar to that of 3.6 µm gauge Mylar. However, the degradation resistance of polycarbonate makes it unsuitable for use with a broad range of chemical classifications. Its use is restricted to chemically unreactive solution specimens or powdered solid sample materials.

Polypropylene and polyethylene are similar in degradation resistance and transmittance properties. These substances are useful for the retention of many types of sample materials and can be used for thin-film sample supports encompassing the entire spectral range. A polyethylene device incorporating both a snap-on ring and thin-film sample support membrane is available from Chemplex Industries, Inc. (Figure 5). This device eliminates the need for separate attachment of a thin-film sample support material with a snap-on ring.

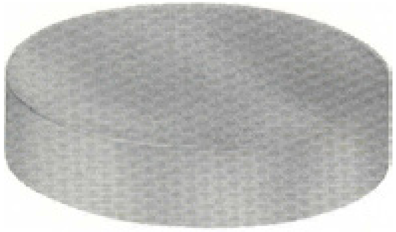

Figure 5 SpectroMembrane® thin-film integrally formed with snap-on ring.

Polyvinylidene chloride (PVC) exhibits a sharp discontinuity in the percent transmittance correlation to analyte-line appearing at 2.8 keV; this represents the K-absorption edge for chlorine. This discontinuity and the substance's unacceptable degradation resistance, make PVC unsuitable for use in XRF sample retention.

Polystyrene exhibits poor degradation resistance, and is thus not suited for use in XRF sample retention. Other materials similarly tested and found to be unacceptable included celluloses, collodian, and nylon. Polyvinyl fluoride is currently being evaluated as a possible material for sample containment.

Gauge Thickness

Uniformity in thin-film thickness is important with respect to minimizing variations in analyte-line transmittance. The process of manufacturing involves gauge control to within approximately ± 10% of nominal thickness. To evaluate the effect of variations in thickness on analyte-line absorption, percent transmittance deviations from a variety of gauges of the same thin-film substance were calculated for a number of analyte lines. Mylar was used since most of the test data were already available.

Results indicated a correlation between percent transmittance deviation units (± %TDU) to decreasing thin-film gauge and increasing analyte-line wavelength. This condition would be most pronounced with very thin-gauge substances and long analyte-line wavelength investigations. For example, a deviation of ±3% TDU was determined for 2.5µm gauge Mylar at an arbitrarily selected analyte line of 12.4 Angstroms. Translation of 36.79 ± 3% transmittance to analyte concentration is insignificant for analytical concern.

Summary

Several parameters pertaining to the suitability of thin-film substances for retaining samples for WDXRF and EDXRF spectrochemical analysis have been described. The materials investigated were all synthetic polymers of various thicknesses, exhibiting differing degradation resistance and analyte-line transmittance. A comparison of percent analyte-line transmittances for thin-film substances and gauges were presented, intended to facilitate selection of a suitable thin-film substance and gauge.

Note 1: Mylar® is a registered trademark of E.I. DuPont de Nemours Co., Inc.
Prolene®, Etnom®, SpectroMembrane® and Chemplex® are registered trademarks of Chemplex
Industries, Inc.

Note 2: Table 1, Degradation Resistance of Thin-Film Substances, is replaced with the most current version.

Note 3: Figure 5. SpectroMembrane thin-film integrally formed with snap-on ring has been replaced with an alternate product of different design and configuration

References

1 SOLAZZI, M.J., "Disposable XRF Sample Cups and Thin-film Sample Supports for X-Ray Fluorescence Analysis," Am. Lab. 16 (11), 72- 78 (1984).

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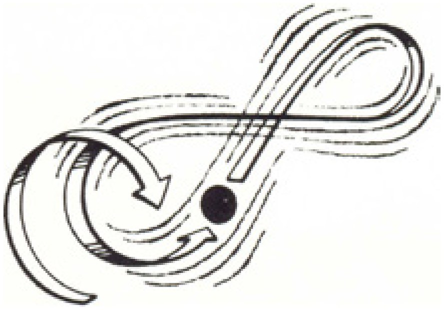
By Dr. Monte J. Solazzi

AN INVESTIGATION OF THE PERFORMANCE OF COMMINUTION VIALS AND BALL PESTLE IMPACT GRINDERS

IN THE PAST, powdered sample materials were comminuted in any available vials by the ball pestle impact grinding technique. The choice of vials used was limited to the familiar flat interior ended medicine-type vials with a selection of screw or snap closures. These grinding containers were not designed or necessarily suitable for providing the reproducible particle size reduction required for high degrees of spectrochemical analytical accuracies. The lack of availability of any other type of comminution vessel and insufficient understanding of the actual events occurring during the comminution process with ball pestle impact grinders, contributed to the popularity of flat interior-ended vials. This paper will discuss particle size reduction of various types of sample materials using SpectroVial® (Chemplex® Industries, Inc.) grinding vials.

Centrifugally accelerated ball pestle and sample
are forced through a figure-eight path of travel.



Background

Chemplex SpectroMill® Ball Pestle Impact Grinder

A ball pestle impact grinder is an electromechanical device designed to rapidly and energetically propel a ball pestle contained in a cylindrical vessel with a powdered sample from one end to the other. The principle of operation of a ball pestle impact grinder is based on the unique behavior of a ball pestle and its effect on a sample. The SpectroMill® ball pestle impact grinder (Figure 1) motivates a ball pestle and sample through a longitudinal figure-eight path of travel that simultaneously rotates in a 360^0 pattern from one end of the grinding vessel to the other (Figure 2). However, as the ball pestle approaches one end of the grinding vessel, the grinder abruptly reverses direction opposed to the travel path of the ball pestle and sample, which increases the intensity of impact. The sample is crushed against the interior ends of the vial by the ball pestle. The cycle is repeated until a predetermined time for attaining a desired particle size has elapsed.

The degree of particle size reduction is related to comminution time, volumetric capacity of the grinding vessel, sample quantity, and type of powdered sample. To control comminution time precisely, the SpectroMill incorporates a 60-min interval timer programmable in increments of 1 min. For repetitive sample preparations, the electronic timer is set to a pre-calculated time. Re-establishing the same comminution time for subsequent sample processing is performed by depressing a reset button located within the timer dial. The unit automatically activates for the previously set time duration. A separate button switch controls manual operation, which overrides the automatic programmable timer.

SpectroMill-II Simultaneously Processes Two Similar or Dissimilar Samples

Flat Interior-Ended Grinding Vials

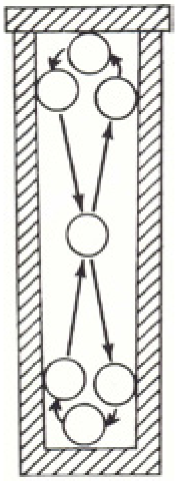


Figure 3. **Traditional flat interior-ended vial with snap cap.**

The flat interior-ended conventional grinding vials form nearly perpendicular angles with the interior walls (Figure 3). The spherical ball pestle cannot crush any sample particles that collect and cohere in these pockets on both ends of the vial. Similarly, the parting line established at the point of conjunction between the vial body and cap presents another area in which sample particles accumulate and avoid comminution. The parting line is usually at the edge of the open side of the vial immediately adjacent to the impact site. Under the thrust of the rapidly moving ball pestle, sample particles are forced and compacted into the crevice formed by the parting line and protected from ball pestle impact. Complicating this issue further, when a disposable plastic grinding vessel is used the closure is generally a completely different and less rigid type of plastic; the vial body is usually rigid polystyrene and the closure is a more pliable polyethylene plastic. The more pliable polyethylene plastic closure becomes momentarily distorted upon impact by the ball pestle and increases the gap of the parting line, and sample particles thus become entrapped and evade the comminution process.

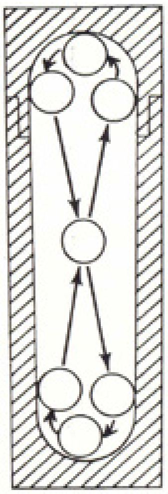


Figure 4. SpectroVials with concaved interior ends in both the vial bodies and closures.

SpectroVial® Comminution Vials

The SpectroVial comminution vial was researched, engineered, and manufactured to serve one specific function: to reduce the sample preparation error for processing powdered samples in ball pestle impact grinders. The vials are cylindrical vessels with concaved interior ends in both the vial bodies and closures (Figure 4). The concaved interior ends form infinite sites to allow impacting and milling to occur, eliminate areas in which sample particles may become entrapped and avoid comminution, and promote intimate particle intermixing since the sample is continuously encouraged to motivate by the figure-eight travel path of the ball pestle. Additionally, the parting line between the vial body and closure is a considerable distance away from the ball pestle impact site to avert the accumulation and compaction of sample particles. Close manufacturing tolerances also limit the gap of the parting line to further reduce the likelihood of sample particle accumulation. In a given cycle, as the ball pestle departs from its arc of travel guided by the radial end of the vial, its rate of speed is centrifugally accelerated. Concurrently, the mechanics of the SpectroMill grinder develops a reversal of direction and imposes a sudden thrust on the ball pestle and sample to further accentuate their speed for impact and milling on the opposite end of the vial. This process continues until the sample is satisfactorily reduced in particle size.

SpectroVials (Figure 5) are manufactured in rigid clear polystyrene plastic with polystyrene friction fitting snap-on caps, and in stainless steel with screw caps fabricated of the same metal for both open ends of the vial body (Figure 6) to facilitate and ensure thorough cleansing. The polystyrene vials are disposable and the stainless steel units are, of course, reusable. Currently under investigation for use as a vial is heat-treated titanium-carbide, which is similar to tungsten carbide in hardness but not brittle and not as expensive to manufacture.

Figure 6
Metal SpectroVials

Figure 5
Disposable polystyrene SpectroVials

Experimental Statistical Analysis

The performance of SpectroVials and flat interior-ended vials was examined by comminuting sand, silicon dioxide, in a SpectroMill programmed for a fixed time duration. The ground sample material for each test aliquot was collimated through a 44 µm screen, collected, weighed, and expressed as a percentage of sample quantity equal to or less than 44 µm in particle size.

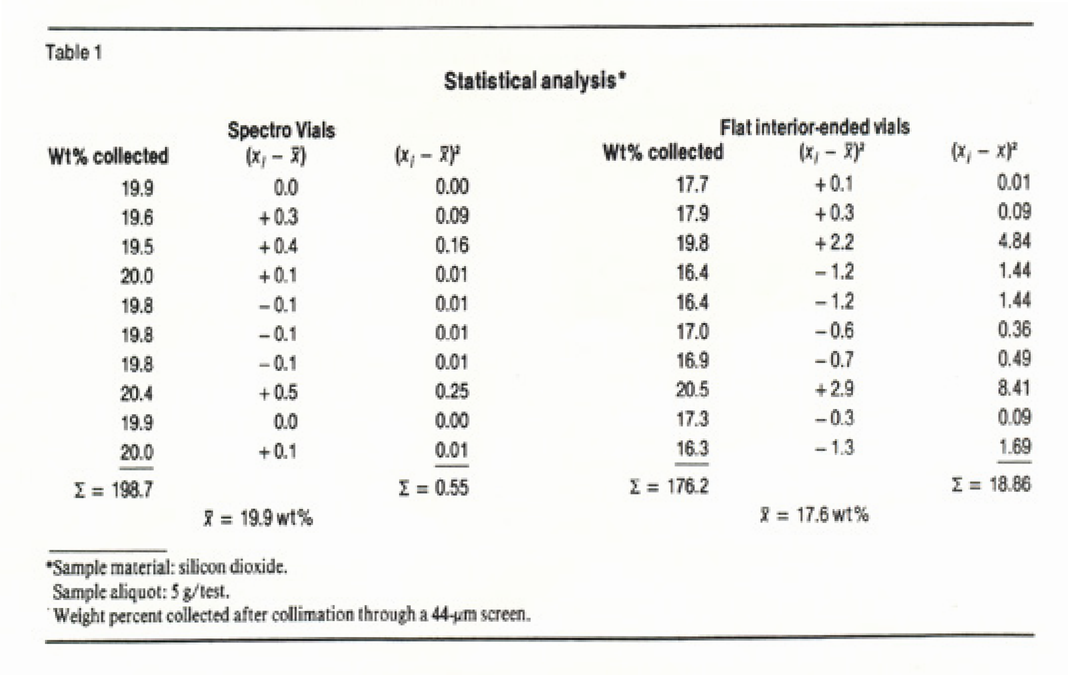


Table 1

Statistical analysis*

	Spectro Vials			Flat interior-ended vials	
Wt% collected	$(x_i - \bar{x})$	$(x_i - \bar{x})^2$	Wt% collected	$(x_i - \bar{x})^2$	$(x_i - x)^2$
19.9	0.0	0.00	17.7	+0.1	0.01
19.6	+0.3	0.09	17.9	+0.3	0.09
19.5	+0.4	0.16	19.8	+2.2	4.84
20.0	+0.1	0.01	16.4	−1.2	1.44
19.8	−0.1	0.01	16.4	−1.2	1.44
19.8	−0.1	0.01	17.0	−0.6	0.36
19.8	−0.1	0.01	16.9	−0.7	0.49
20.4	+0.5	0.25	20.5	+2.9	8.41
19.9	0.0	0.00	17.3	−0.3	0.09
20.0	+0.1	0.01	16.3	−1.3	1.69
Σ = 198.7		Σ = 0.55	Σ = 176.2		Σ = 18.86
	$\bar{x}$ = 19.9 wt%			$\bar{x}$ = 17.6 wt%	

*Sample material: silicon dioxide.
Sample aliquot: 5 g/test.
˙Weight percent collected after collimation through a 44-µm screen.

Sand was selected as the experimental material for this application for several reasons: relative hardness and resistance to particle size reduction particularly in polystyrene vessels; initial coarse particle size of 149 µm with only 5 wt% passing through a 44 µm screen; and abundance of sample material for similar comparisons. Disposable polystyrene SpectroVials with a volumetric capacity of 30 ml and comparable flat interior-ended vials and two methyl methacrylate 11 mm diameter ball pestles were used for each test sample. The SpectroMill was programmed for automatic operation with a comminution time of 25 min for processing each test aliquot. After each completed grinding cycle, the comminuted samples were weighed and sieved. The collected amounts were again weighed and expressed as percentages of material passing through a 44mm screen. Ten replicate 5-g sand samples were processed in polystyrene SpectroVials and a duplicate test series was similarly prepared in polystyrene flat interior-ended polystyrene vials. A statistical analysis was performed to determine the variations in processing both groups of samples. The data are tabulated in Table 1, and Eqs. (1) and (2) were used to calculate the standard deviation, a, and coefficient of variation, v, for each test group. Table 2 shows the calculated variations for the SpectroVial and flat interior-ended vials.

$$\sigma = \sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2/(n - 1)} \qquad (1)$$

where a = standard deviation
Xi = the ith individual value
n = number of observed values
x = arithmetic mean.

Examination of the data demonstrates the excellent performance and reliability of SpectroVials in statistically reproducing the weight percent quantity of test material collimated through a 44-µm screen, 19.9% ± 0.25, and the poor performance of flat interior-ended vials, 17.6% ± 1.5.

Comparison Study

The experiment with silicon dioxide was extended to include evaluation of the effects on particle size by varying processing time, grinding media, and sample quantity. This investigation used two stainless steel SpectroVials® of different volumetric capacities and disposable polystyrene SpectroVials. The parameters tested for each group were varied.

The first test group used a 90-ml stainless steel SpectroVial, 66 mm long x 54 mm in diameter, and contained a 15-g sample for each test. Because of the sample quantity employed, two stainless steel ball pestles of 12.7-mm diameter were used. The first sample was processed for 10 min and subsequent samples were ground in increasing 10-min increments. The wt% of ground silicon dioxide passing through a 44 µm screen was calculated (Table 3) and plotted against processing time (Figure 7). The data show excellent correlation and illustrate that within a 30-min cycle, 95.9 wt% of silicon dioxide is equal to or less than 44 µm in particle size.

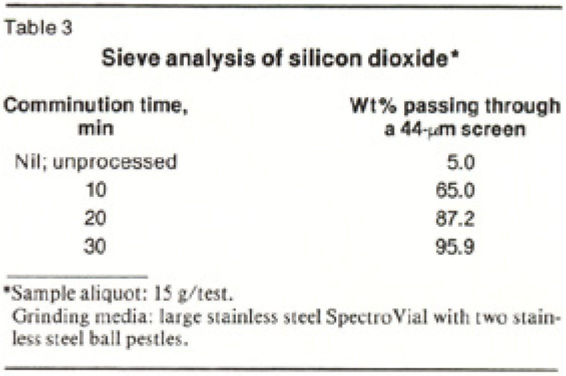
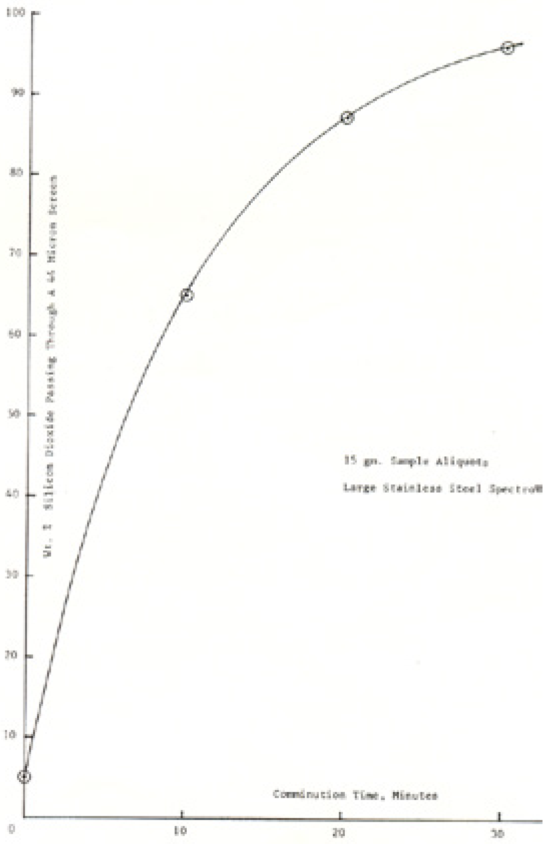


Table 3

Sieve analysis of silicon dioxide*

Comminution time, min	Wt% passing through a 44-µm screen
Nil; unprocessed	5.0
10	65.0
20	87.2
30	95.9

*Sample aliquot: 15 g/test.
Grinding media: large stainless steel SpectroVial with two stainless steel ball pestles.



Figures 7–9 *Comminution analyses of wt% of ground silicon dioxide passing through a 44-µm screen plotted against processing time.*

The second test group consisted of 5-g aliquots comminuted in a 35-ml stainless steel SpectroVial, 76 mm long x 33 mm in diameter, containing one 11-mm-diameter stainless steel ball pestle. It was also determined that a 5-g sample aliquot was adequate to present for spectrochemical analysis. The small size SpectroVial was commensurate with the smaller quantity of sample material processed. This group of samples was processed in increments of 5 min up to 15 min and collimated. Within a I5-min processing time, 96.2 wt% passed through a 44 µm screen. The data for this study also display excellent correlation, as tabulated in Table 4 and illustrated in Figure 8.

The last test group in this series also involved 5-g silicon dioxide sample aliquots. For this application, however, disposable polystyrene SpectroVials, 75 mm long x 33 mm in diameter, and two 11-mm diameter methyl methacrylate ball pestles were used as the grinding media. Varied processing times were selected for individual tests up to 45 min and the wt% passing through a 44µm screen was calculated (Table 5). The weight percent of comminuted sand passing through the screen representative of the arithmetic mean, X, of 19.9 wt% was taken from the statistical analysis section (Table 1) to evaluate its position in the drawn curve relative to the other points. Figure 9 demonstrates excellent correlation, including the point inserted from Table 1 (19.9 wt%).

Other Material Investigations

The Applications Laboratory at Chemplex Industries, Inc. is frequently presented with a variety of sample materials submitted from different sources for evaluation. The following section briefly describes several experiments of various types on different materials that were difficult to process. In each example, SpectroVials were used.

Table 4

Sieve analysis of silicon dioxide*

Comminution time, min	Wt% passing through a 44-μm screen
Nil; unprocessed	5.0
5	60.8
10	86.2
15	96.2

*Sample aliquot: 5 g/test.
Grinding media: medium size stainless steel SpectroVials with one stainless steel ball pestle.

Table 5

Sieve analysis of silicon dioxide*

Comminution time, min	Wt% passing through a 44-μm screen
Nil; unprocessed	5.0
25[a]	19.9[a]
35	25.0
45	30.0

*Sample aliquot: 5 g/test.
Grinding media: large polystyrene SpectroVial with two methyl methacrylate ball pestles.
[a]These data were taken from the statistical analysis section, Table 1.

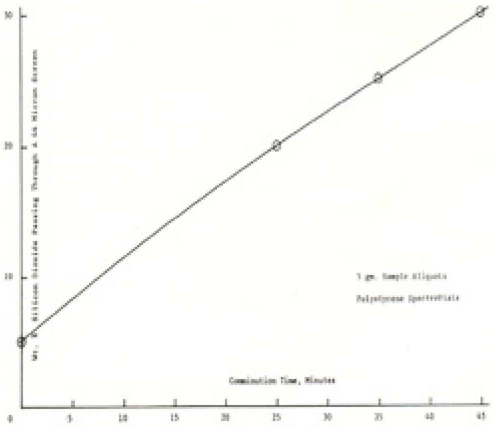
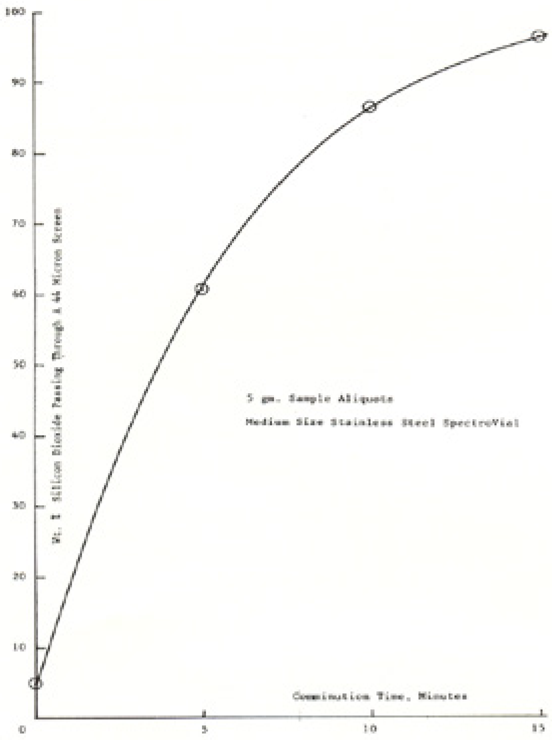


Figure 9

Figure 8



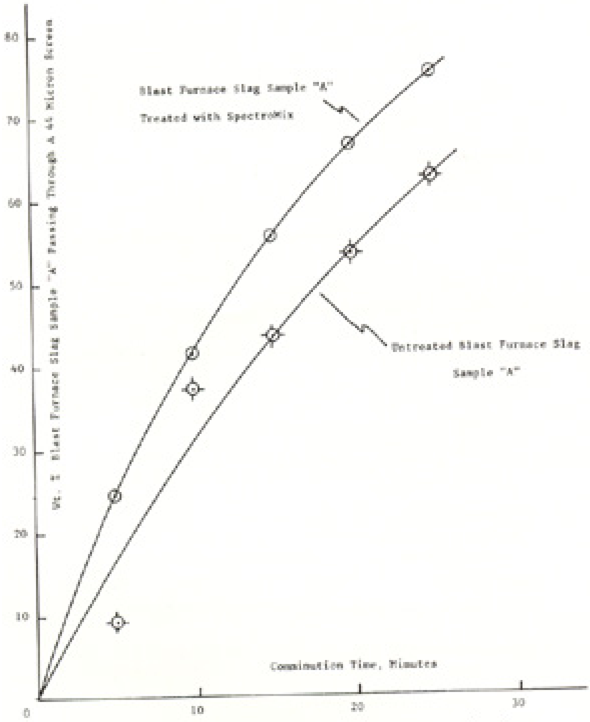


Figure 10 *Comminution analysis of slag sample A.*

Blast Furnace Slags

Three blast furnace slag samples were submitted for a suggested sample preparation procedure. A typical analysis of the major constituents was disclosed as follows: 24% SiO_2, 39% CaO, 7% Fe_2O_3 10% MgO, 10% MnO, and 7% Al_2O_3). The samples were received in chunks of approximately 0.5 x 0.5 x 2 cm. Two of the slag samples, which will be identified as A and B, were occluded with steel balls ranging in size up to approximately 2 mm in diameter. The third sample, C, was relatively free of foreign metallic occlusions. By weight, samples A and B contained approximately 96% and 2% steel balls, respectively; none were detected in sample C.

The difficulty in processing these three samples was related to the unwanted presence of the occluded metallic balls. In the form received, the blast furnace slag samples were unsuitable for standard comminution procedures. The chunks were first de-agglomerated with a mallet and the steel balls were removed using a magnet. The average chip size was approximately 2 x 2 x 3 mm. To ensure complete occluded steel ball removal, each sample was subjected to a 2-min process in the SpectroMill using a stainless steel SpectroVial. The extraneous steel balls were again magnetically removed.

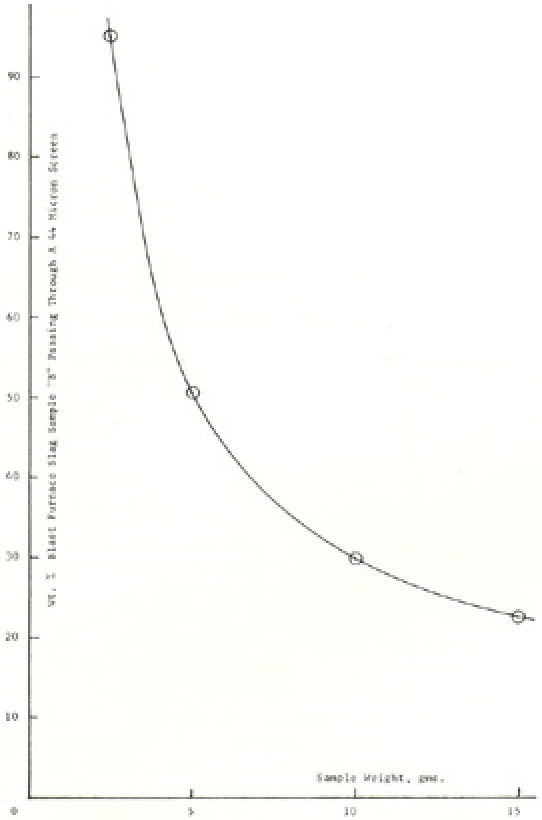


Figure 11 *Comminution analysis of slag sample B.*

A 15-g aliquot of sample A, which contained the greatest quantity of occluded steel balls, was comminuted in a 66-mm long x 54-mm diameter stainless steel SpectroVial with two 12.7-mm diameter ball pestles in increments of 5 min. up to 25 min. After each grinding cycle a 1-g aliquot was removed for sieving through a 44 µm screen and the quantity collimated was weighed and expressed as a weight percent.

Both factions of the removed 1-g aliquot were returned to the vial for further comminution. *Table* 6 shows the data for this sample preparation procedure and *Figure 10* provides a graphic illustration. Inspection of the data shows an unsatisfactory distribution of points surrounding the best-drawn curve. It was suspected that the sample particles during the comminution process were not adequately intermixing for ball pestle impact. The experiment was then repeated, but this time a 0.5-g SpectroMix™ grinding/briquetting aid was added to the 15-g sample in pre-measured capsule form.

Table 6

Sieve analysis of blast furnace slag A*

Comminution time, min	Wt% passing through a 44-µm screen
5	9.1
10	37.1
15	43.4
20	53.2
25	62.5

---

*Sample aliquot: 15 g with 1 g removed for sieving after each 5-min interval; collimated and residual factions combined with original aliquot for subsequent processing.

Table 7

Sieve analysis of blast furnace slag A processed with SpectroMix*

Comminution time, min	Wt% passing through a 44-µm screen
5	24.8
10	41.4
15	55.6
20	66.5
25	75.0

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*Sample aliquot: 15 g; same as in Table 6.
Sample-to-SpectroMix ratio = 30 : 1.

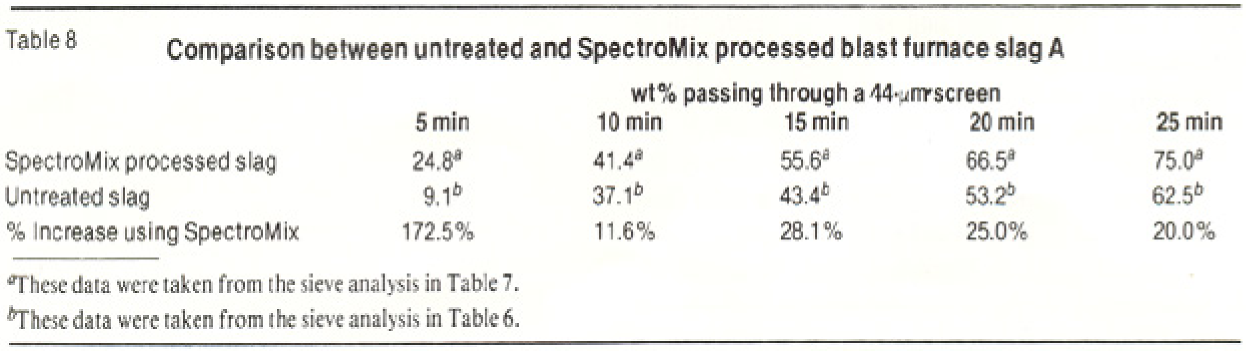

Table 8

Comparison between untreated and SpectroMix processed blast furnace slag A

	wt% passing through a 44-µm screen				
	5 min	10 min	15 min	20 min	25 min
SpectroMix processed slag	24.8[a]	41.4[a]	55.6[a]	66.5[a]	75.0[a]
Untreated slag	9.1[b]	37.1[b]	43.4[b]	53.2[b]	62.5[b]
% Increase using SpectroMix	172.5%	11.6%	28.1%	25.0%	20.0%

[a] These data were taken from the sieve analysis in Table 7.

[b] These data were taken from the sieve analysis in Table 6.

Examination of the data in *Table* 7 shows a significant improvement in results and excellent graphic correlation (Figure 10). Both of the curves were plotted in the same graph to provide a better view of the improvement relative to the untreated sample. To further illustrate the improvement in particle size reduction realized with SpectroMix, a comparison between untreated and SpectroMix processed blast furnace slag sample A was performed *(Table* 8). The data were taken directly from Tables 6 and 7, and the percentage increase of collimated material in relation to each period of processing was calculated. The use of the grinding aid also facilitated cleansing operations because of its lubricious nature and reduced the procedure to a simple dry paper towel wipe.

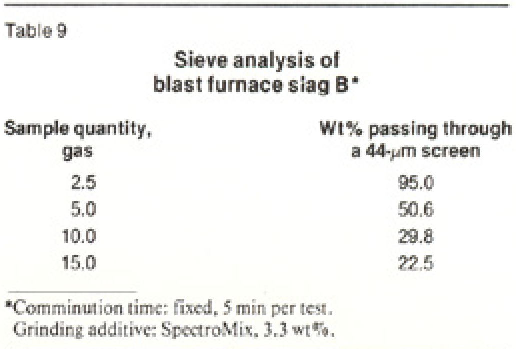

Table 9

Sieve analysis of blast furnace slag B*

Sample quantity, gas	Wt% passing through a 44-µm screen
2.5	95.0
5.0	50.6
10.0	29.8
15.0	22.5

*Comminution time: fixed, 5 min per test.
Grinding additive: SpectroMix, 3.3 wt%.

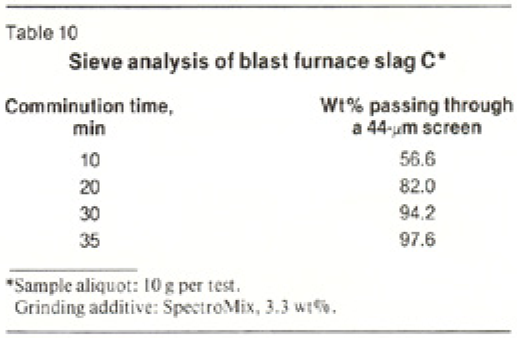

Table 10

Sieve analysis of blast furnace slag C*

Comminution time, min	Wt% passing through a 44-µm screen
10	56.6
20	82.0
30	94.2
35	97.6

*Sample aliquot: 10 g per test.
Grinding additive: SpectroMix, 3.3 wt%.

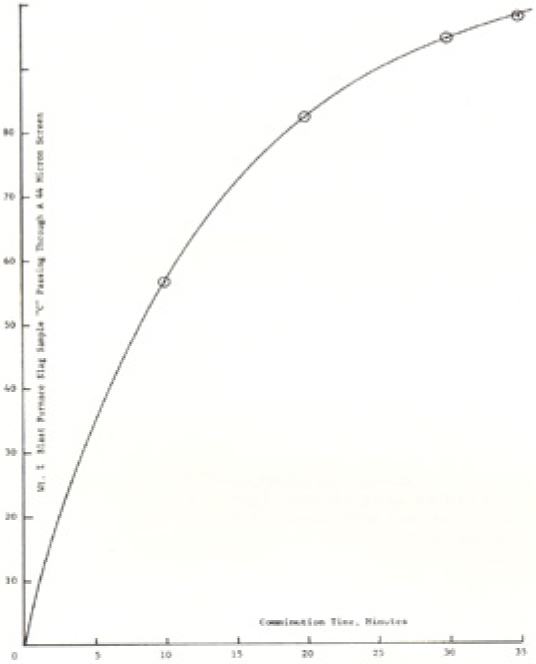

Figure 12 *Comminution analysis of slag sample C.*

Sample B was used to illustrate the effect sample quantity had on particle size. The SpectroMill was programmed for a 5-min comminution cycle per test. The same stainless steel SpectroVial was again used. SpectroMix powder was added to each sample aliquot in a proportion of 3.3 wt%. Four test samples of 2.5, 5, 10, and 15 g were prepared. *Table* 9 shows the reduction in the weight percents of collimated materials with increasing sample quantity. *Figure* 11 displays excellent correlation of the plotted points and demonstrates the effect of sample quantity on particle size.

The last blast furnace slag, sample C, was similarly processed with 3.3 wt% SpectroMix and was used to determine the length of comminution time required to yield at least 95 wt% of collimated material passing through a 44-µm screen. The same stainless steel vial and ball pestles were used to keep variables to a minimum. Each sample aliquot tested was 10 g. The data presented in *Table 10* show that approximately 30 min was sufficient to grind the sample to a particle size in which 95 wt% passed through the 44 µm screen. *Figure* 12 displays the excellent correlation between each of the plotted points.

Tin Ores

The study of tin ores was particularly interesting because the analyst had already established a viable sample preparation procedure and was exploring the possibility of incorporating the SpectroMill and SpectroVials in the scheme. Specific conditions were outlined. Fixed quantities of sample (2 g) and a grinding additive (12 g) had to be maintained. Evaluation consisted of determining the length of time required for each 14-g sample/additive mixture to furnish a particle size in which at least 95 wt% passed through a 44-µm screen. Seven tin ore specimens were submitted for study. A 66-mm long x 54-mm-diameter stainless steel SpectroVial with two 12.7-mm-diameter stainless steel ball pestles were employed as the grinding media. Each tin ore specimen was processed in the ball pestle impact grinder, sieved, and the collected quantity expressed as weight percent. *Table* 11 shows the results of this study; a processing time of 35 min was adequate to comminute the tin ores to the desired particle size.

Table 11

Wt% passing through a 44-µm screen

Sample no.	15 min	30 min	35 min (extrapolated)
1	68.8	93.8	99.5
2	65.3	93.8	100
3	69.0	93.1	98.3
4	70.0	93.6	98.0
5	70.1	93.2	98.0
6	63.9	90.5	97.0
7	60.3	89.2	95.5

Firebrick

A single firebrick was submitted for comminution analysis. The only requirement was not to exceed a processing time of 5 min to achieve a particle size of equal to or less than 44 µm. A 76-mm-long x 33-mm-diameter stainless steel SpectroVial with two 11-mm diameter ball pestles was used as the grinding media. The sample aliquot per test was 5 g after the firebrick was pulverized. According to the data in *Table* 12, within a 5-min comminution cycle 96.3 wt% of the sample passed through a 44 µm screen. *Figure* 13 illustrates the distribution of points.

Table 12

Sieve analysis of fire brick*

Comminution time, min	Wt% passing through a 44-µm screen
1.0	69.9
2.5	89.5
5.0	96.3

*Sample aliquot: 5 g/test.

Figure 13 *Comminution analysis of fire brick.*

Summary and Conclusion

The effectiveness of SpectroVials in comminuting samples in a ball pestle impact grinder in preparation for spectrochemical analysis has been demonstrated. The data presented in Table 1 and Table 2 illustrates the higher degrees of precision and increased particle size reduction obtained with SpectroVials. The improvement in reproducibility is attributed to the concaved interior ends in both sides of the vial, the smooth unobstructed interior walls, and the displacement of the point of conjunction between the vial body and closure from the impact site. During comminution, individual sample particles are unable to elude ball pestle impact by virtue of the interior radial ends and the absence of pockets or crevices for sample material to collect. The resultant comminuted sample is homogeneously blended and uniformly reduced in particle size and distribution with a savings in processing time.

SpectroVials are available in different volumetric capacities in both polystyrene plastic and stainless steel to permit a comprehensive range of sample material processing. The future use of heat-treated titanium-carbide materials may extend the range of sample material processing and reduce comminution time while avoiding the brittle nature and high manufacturing costs of tungsten carbide. With the use of the SpectroMill, the analyst can precisely control particle size reduction by varying cycle time and sample charge.

The investigations described in this paper illustrate the success of SpectroVials in reducing sample preparation error. The range of sample materials that can be processed with SpectroVials is extensive, and the examples cited demonstrate typical superior performance in the comminution process.

Note: SpectroMill®, SpectroVial®, SpectroMix® and Chemplex® are registered trademarks of Chemplex Industries, Inc.

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By Dr. Monte J. Solazzi

Comminution Device for X-Ray Spectrochemical Analysis

SAMPLE SUBSTANCES ranging from single to multiple-compound structures, classified as compositionally complex in this article, comprise combinations of different particles. Each is characterized by its separate chemical and physical properties, e.g., chemical composition, particle size, shape, hardness, and density. In practice, this is a fair representation of the samples generally presented to the analyst for direct X-ray spectrochemical analysis, and as such, they are not acceptable. Any differences or variation in the constituent sample particles with respect to chemical and physical properties are potential factors affecting the X-ray data and degree of analytical accuracy. Comminution reduces these discrepancies to minimal levels.

The objective of the comminution procedure is to reduce the constituent particles to a uniform size, shape, distribution, and level of insignificant influence on analytical data in a statistically reproducible manner. The comminution equipment must be capable of utilizing a single set of operating conditions common in meeting this objective, regardless of initial differences in sample composition complexities and physical characteristics. This imparts a high degree of credibility to the sample preparation procedure with the foreknowledge that each type of sample substance is effectively comminuted. The comminution equipment must also be relatively fast and simple to operate, maintain pace with current and future laboratory needs, and be ergonomically designed to minimize operator discomfort, especially for routine sample processing. The comminution equipment must also provide a means to minimize the introduction of transition wear-element contamination to the sample substance and wear to the grinding vessel and media. The GyralGrinder® (Chemplex® Industries, Inc.), a comminution device featuring variable frequency and intensity of impact control, meets these requirements.

Principle of Operation

Figure 1
Comminution Vessel

The GyralGrinder is an electromechanical device that imparts an eccentric gyral motion to a comminution vessel containing a sample substance and freely mobile grinding media *(Figure* 1). The eccentric gyral motion is created by inertia of the mechanics of the system to generate a controlled imbalance condition resulting in an energetic motivation of the grinding vessel. Comminution is effected by collision and milling actions by the grinding media on the sample substance.

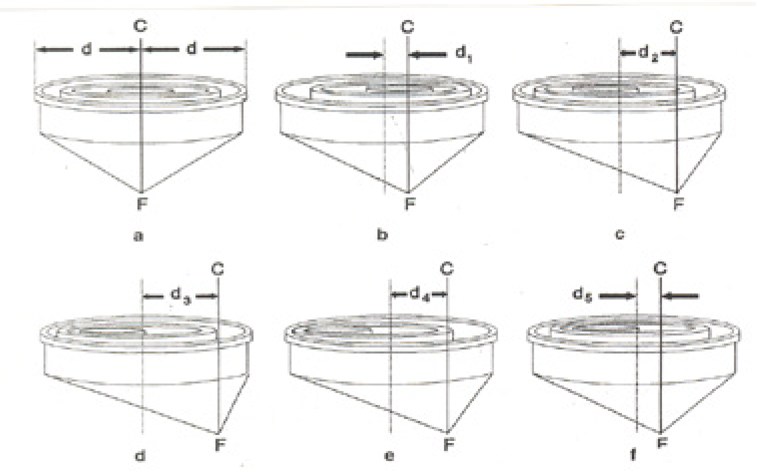

Figure 2 *Typical gyral motion of comminution vessel.*

Figure 2 illustrates a grinding vessel located a distance (d) from a focal point (F) relative to the center axis of the system (C). At rest (Figure *2a),* the comminution vessel together with its grinding media and sample are stationary (the grinding media are shown to be in center alignment with the center axis of the system for illustrative purposes). As a moment is initiated by the mechanics of the system pivoting at the focal point F, Figure *2b,* the grinding vessel is laterally displaced a distance (d,) from the center vertical axis (C); the grinding media and sample generally lag behind the grinding vessel displacement direction as they are propelled by its trailing side. Subsequent increases in instability, Figure *2c,* gyrally enlarge the displacement distance (d2) of the grinding vessel relative to the' center vertical axis up to a physical limitation imposed by other mechanics integrated in the system. At the limitation displacement distance (d]), Figure *2d,* of the grinding vessel, the mechanics gyrally reverse displacement direction accompanied by a corresponding decrease in displacement distance 4), Figure *2e,* in a circular arc configuration (not shown). The grinding elements, however, continue in the same initial travel path with increased speed and inertia propelled by the trailing side of the grinding vessel to impact its interior walls. The reversal of grinding vessel direction in the oncoming path of the sample substance and grinding media is extremely energetic and is primarily responsible for comminution. The cycle repeats itself in the opposite direction, Figure *2f.* Furthermore, the reversal of displacement direction of the grinding vessel in a circular arc adds a milling effect to the sample substance created by the grinding media that acquires a spin attributed to the gyral mechanics.

The mechanics of operation are portrayed in slow motion to illustrate the principles involved in this equipment. In practice, the comminution process is extremely rapid and highly energetic. Additionally, by the introduction of control on the number of displacement distance occurrences within an interval of time, the frequency and intensity of impacts become variable. This feature provides the analyst with the capability *of* adjusting the comminution process to range from a simple gentle grind to a most vigorous and energetic action.

Most importantly, independent operator control of intensity and frequency of impact, together with other features incorporated in the device reduce the comminution process to the use of a common set of operating parameters applicable to all sample substances regardless of their dissimilarities in composition complexity and physical characterization. Control over the frequency and intensity of impact level ensures that transition wear-element contamination to the sample is significantly minimized; in addition to reduced wear to the comminution vessel and grinding elements.

Experimentation

A series of experiments were conducted relating to particle size weight fractions collected from comminuted sample material processing. Four different arbitrary sample substances were selected principally for their relative dissimilarities in composition complexity and physical characterization.

The GyralGrinder can be operated in several different modes: intensity of impact held constant and processing time varied, processing time held constant and intensity of impact varied, and both processing time and intensity of impact varied. A typical representation of the comminution process and experiments to be performed in this report is shown in *Figure* 3. This relates the particle size weight fraction of the sample collected corresponding to either processing time, intensity of impact, or both. The degree of curvature appearing at the upper end of the curve represents the range at which no further particle size reduction is realized with additional processing for a specific sample material substance, comminution vessel material, and equipment.

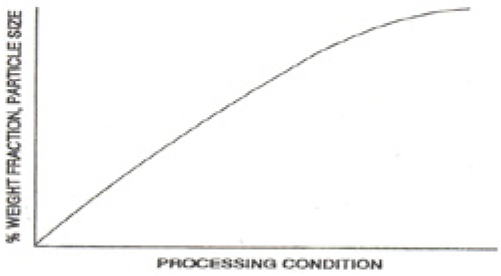

Figure 3 *Particle size versus processing time, intensity of impact on comminution vessel substance.*

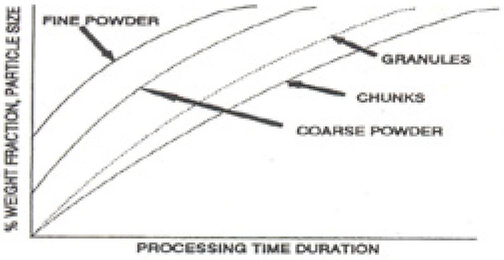

Figure 4 *Typical ineffectiveness of tradional comminution equipment.*

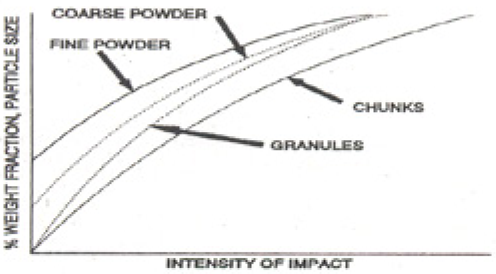

Figure 5 *Improvement in the comminution process attributed to varied intensity of impact settings.*

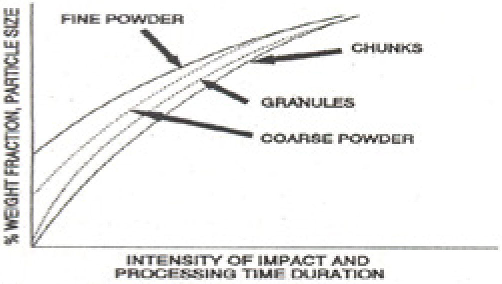

Figure 6 *Comminution effectiveness under a common set of conditions in processing sample substances of dissimilar chemical and physical characterization.*

Varied Processing Time

The device was operated without benefit of utilizing the variable intensity of impact control, which, in principle, is similar to the operational performance of traditional comminution equipment. Each sample substance was processed for specified time duration and its respective particle size weight fraction collected as previously described. The results of this test are exhibited graphically in *Figure* 4. As expected, the fine powdered substance required less processing time in producing the greatest percentage of collected comminuted particles. Sample substances initially presented in chunk physical form dictated the longest processing time in generating similar particle sizes. The notation that all curves are widely separated and do not converge is clearly reflective of the dissimilar behavior of different sample substances when subjected to the same processing conditions. Most importantly, this illustrates that the operating conditions employed for a given classification of sample substances are not presumably translatable to another without implementing operational adjustments.

Varied Intensity of Impact

An experiment was performed that involved holding processing time fixed and varying intensity of impact, as shown in *Figure* 5. A significant improvement in the comminution, process is indicated by the convergence of the individual curves to a point common to the different sample substances with the exception of the chunky sample material, which still presented difficulty as evidenced by its displacement and degree of departure from convergence with respect to the other curves. Ideally, curves generated by dissimilar sample substances should decrease in their displacement from each other and converge at some common point. A common point of convergence represents the highest degree of effectiveness in the process realized for given sample substances, comminution vessel material, and grinding equipment. It is indicative of applying a single set of operational parameters common to all sample substances within the range of analytical interest.

Varied Processing Time and Intensity of Impact

The last experiment was reflective of the instrument's ability to process sample substances of varied compositional complexity and physical characterization. For this test, both processing time and intensity of impact were varied. A GyralGrinder operated in this manner incorporates the benefits of both varied comminution time and intensity of impact processes into a common set of operating parameters. The results of the test are represented in *Figure* 6. The convergence of all curves at approximately the same point common to all the sample substances clearly demonstrates the comminution effectiveness of the device. The improvement in the comminution process is directly attributed to the use and application of the intensity and frequency of impact control. As illustrated, this feature provides a common set of operating conditions at which virtually any type of sample substance, regardless of dissimilarities in chemical composition and physical properties, is uniformly processed. The resultant sample substances are similar in particle size and homogeneously distributed for improved statistical precision and analytical accuracy for direct X-ray spectrochemical analysis.

Comminution Vessels

Selection of the most appropriate comminution vessel substance is determined by material hardness, for further maximizing of the comminution process and avoidance of transition wear-element contamination to the sample. The tests in this study were performed in a hardened steel comminution vessel, which will satisfy most laboratory applications, and is supplied as a standard item with the instrument. Typical wear-element contamination from a hardened steel comminution vessel is caused by iron, chromium, silicon, manganese, and carbon. It is reasonably resistant to abrasion and very durable for moderate to high intensity and frequency of impact settings.

For applications requiring a harder grinding vessel substance and avoidance of transition wear element contamination attributed to hardened steel, different and harder vessel substances are optionally available. They include tungsten carbide, alumina ceramic, and zirconia ceramic. Generally, a harder comminution vessel material results in shorter processing times and decreased intensity of impact level settings. Empirical investigations and testing similar to those described in this presentation are generally required prior to actual sample substance processing and with each change in comminution vessel material. This procedure will assist in determining the optimum common operating parameters to accommodate the expected types or classifications of samples submitted for X-ray spectrochemical analysis. Once these common conditions are empirically determined and established, they should remain reasonably constant for all subsequent similar sample material processing.

Instrument Features

The GyralGrinder is a freestanding unit at an average determined height intentionally selected to reduce operator bending and fatigue. The operating controls are conveniently located in the top lid cover, which is supported by dual pressurized gas springs, and lifts upward and back out of the way. This enables close access to the grinding vessel chamber in a standing position. With the lid cover in the closed position, the controls are also within easy reach, are spatially located in groups of function similarities, and are accessible in a standing position.

Comminution Vessel Clamping Mechanism

The comminution vessel clamping mechanism employs a uniquely engineered single-handle cam-operated lever locking design that pivots out of the way. This greatly facilitates removal of the comminution vessel and further provides unobstructed access to the comminution vessel chamber in a standing position. The critical components in the clamping mechanism are fabricated from hardened chrome steel for extended longevity of use. A dust rail is also incorporated within the comminution vessel chamber that serves to collect any residual powdered sample substances, maintains the gyral mechanics relatively dust free, and facilitates cleanup of inadvertent spills.

Controls

All operating controls are located on the exterior of the lid cover. They include a lighted push-button Main switch, a lighted pushbutton manual On/Off switch, a lighted push-button Momentary Operation switch, a control for the intensity of impact, and a programmable electronic interval timer in I-min increments. The push-button switches are also illuminated in different color codes for further ease of identification. The Main switch supplies power to the unit. The Manual switch is employed to operate the unit without a fixed, timed processing interval. The Momentary switch engages the unit for as long as this control is held down in the "On" position. The timer is programmable for fixed time durations in processing sample substances for similar time intervals in 1-min increments. The device utilizes solid-state electronics and controls, which are also located in the lid cover.

Miscellaneous Features

The instrument is constructed of heavy gauge steel and is electro statically coated with a durable finish. It incorporates sound-absorbing material to reduce noise generation to acceptable limits, casters for intermediate mobility to the installation site, and skid-resistant leveling legs to account for irregularities in flooring. Safety switches and lid cover locking devices are also incorporated.

Conclusion

By the introduction of operator-controllable variable intensity and frequency of impact to powdered sample material comminution, innumerable types of sample substances of varying chemical compositionally complexity and physical characterization are effectively and similarly comminuted by the utilization of a single common set of operating parameters. Transition wear-element contamination to the sample substance and wear to the comminution vessel and components are significantly minimized by controlling displacement distances and frequency of impact occurrences, within an interval of time and associated intensities. Other features incorporated in the instrument are intended to greatly facilitate the comminution process concurrent with providing ease of operation for the analyst.

GyralGrinder® and Chemplex® are registered trademarks of Chemplex Industries, Inc.

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