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Chemistry

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MASTER

PRESSING POWDER SAMPLES FOR SPARK-SOURCE MASS SPECTROGRAPHIC ANALYSIS

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT Contract W-7405 eng 26**

UNION CARBIDE

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ABSTRACT

Two methods have been developed for pressing powder samples for mass spectrographic analysis. Both methods involve isostatic pressing of the sample, with or without an electrically conducting support medium, in a naphthalene mold. The methods have been applied to a wide variety of matrix materials, both conducting and insulating, and have been found to be structurally effective about 98 percent of the time. The pressure vessel in which the samples are pressed uses a mineral oil pressing fluid and provides pressures in the range of 30,000 to 180,000 psi.

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SUMMARY

Approximately 25 percent of all samples for spark-source mass spectrographic analysis of impurities are received in powder form. Methods have been devised for pressing these powders into rods suitable for analysis.

The two methods used in the preparation of powders for spark-source mass spectrographic analysis are variations of a pressing technique on which a patent has been received under the title "Isostatic Pressing of Product Having a Large Length-to-Diameter Ratio".(1) The two methods used in this laboratory are referred to as "true isostatic pressing" and "radial or unilateral pressing".

INTRODUCTION

Preparing powder samples for spark-source mass spectrographic analysis is as important as any single phase of trace impurity determination. The method used can play a major role in the final results obtained due to contamination and plate interpretation. Also, if the sample is to be rendered suitable for high vacuum sparking, it must be electrically conducting or semiconducting and must have sufficient physical strength to allow the sample to be clamped in the ion source.

Two techniques of preparing powders for mass spectrographic analysis have been used in this laboratory, namely: sample pressing and dissolution. Best results have been obtained by the pressing method.

PRESSING PROCEDURE

INTRODUCTION

The methods used in this laboratory to prepare powders (either compounds, metals, alloys, or mixtures) for spark-source mass spectrographic analysis are variations of a pressing technique to which a patent has been granted. The title of this patent is "Isostatic Pressing of Product Having a Large Length-to-Diameter Ratio".(1) Two methods will be discussed: (1) true isostatic pressing, and (2) radial or unilateral isostatic pressing.

PRESSING METHODS

True Isostatic Pressing

A naphthalene mold is prepared in a die, shown in Figure 1. This naphthalene mold is removed from the die, loaded with the sample, and capped with naphthalene.

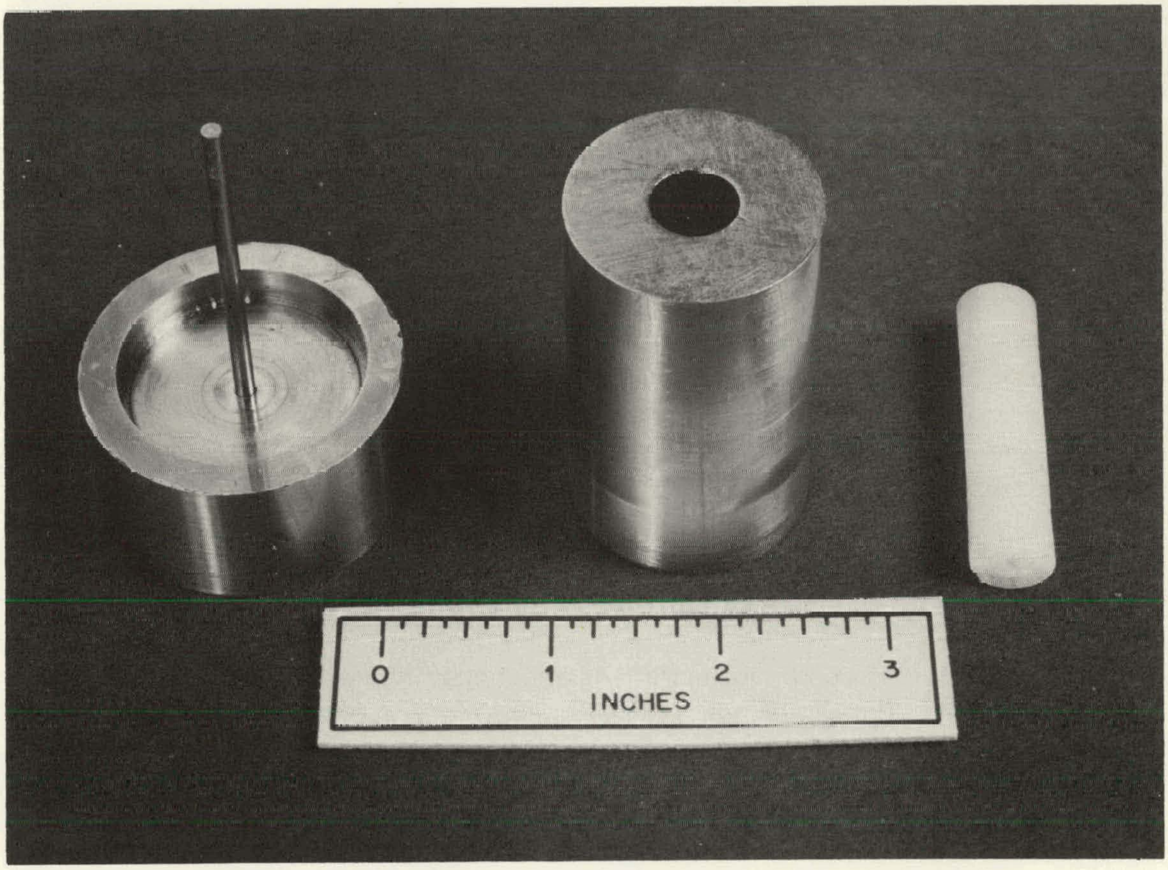

Figure 1. NAPHTHALENE MOLD AND DIE ASSEMBLY.

Loading the mold is done in a Teflon-lined hood, shown in Figure 2. The Teflon liner permits quick detection of visible contaminants and facilitates the maintenance of ultra clean surfaces.

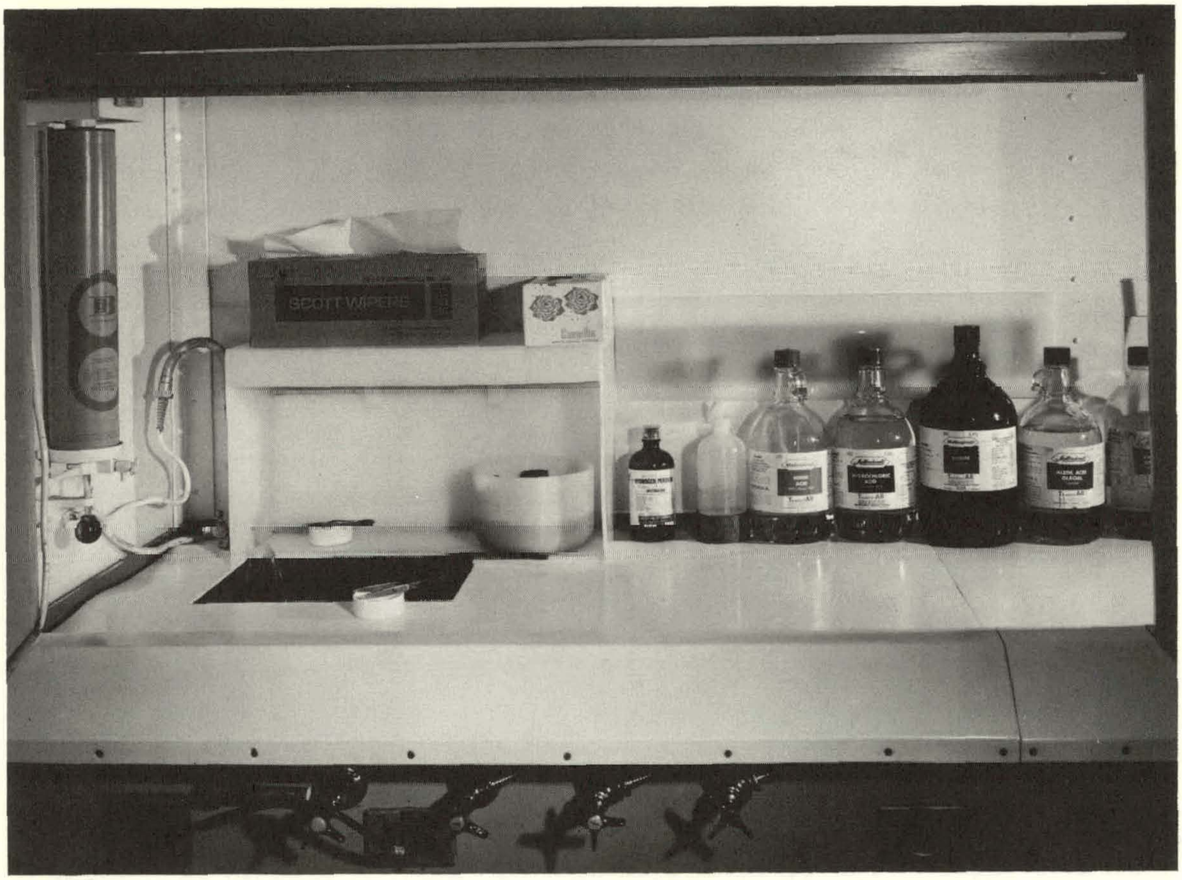

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Figure 2. TEFLON-LINED HOOD.

The capped mold, containing the powder, is then placed in a rubber fingercot and evacuated. This evacuated container is then sealed and placed in the pressure vessel, seen in Figure 3, and pressed at 30,000 psi. After the rod has been pressed, the naphthalene is removed with acetone or by sublimation with hot air. The sample rod is then stored in a vacuum oven until ready for use.

All melting, pouring, and sublimation of the naphthalene is done in a glove box, seen in Figure 4. The glove box is used simply to prevent the naphthalene vapor from spreading throughout the laboratory and to decrease the chances of contamination. Figure 5 presents another view of the glove box showing the equipment needed for mold preparation.

This pressing method has been applied to many sample types—both insulators and conductors. When pressing most nonconducting materials, the sample is mixed with a

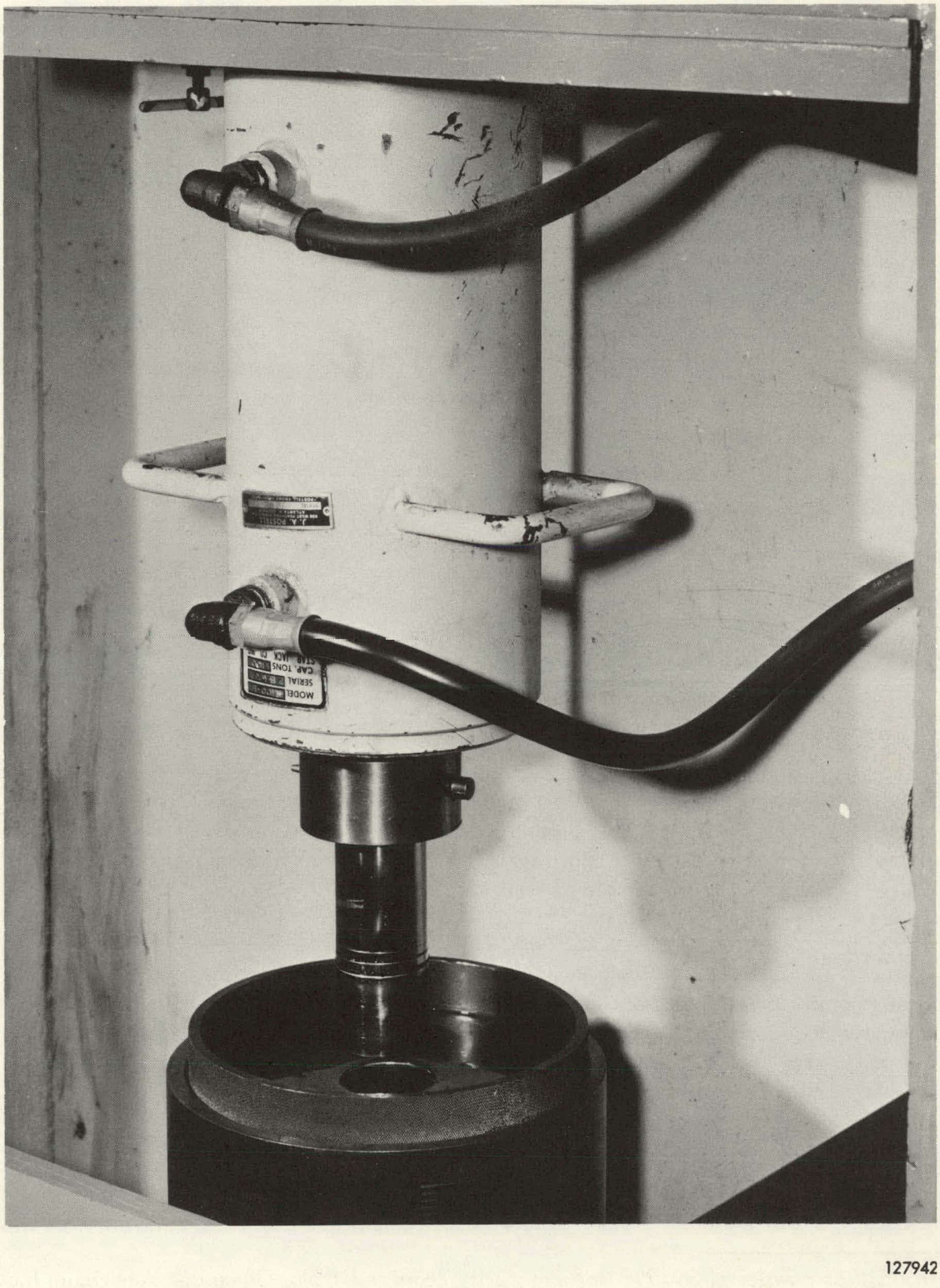

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Figure 3. PRESSURE VESSEL.

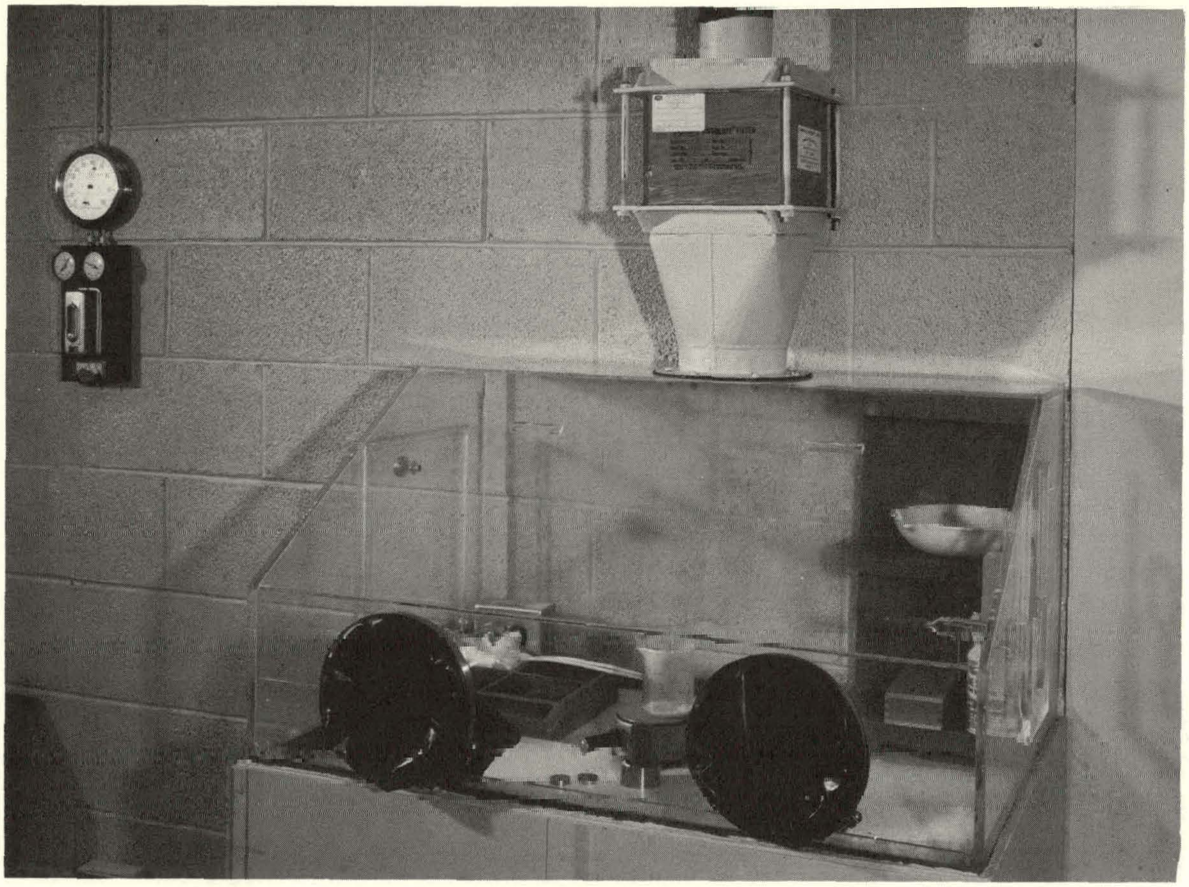

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Figure 4. GLOVE BOX.

pure silver powder[(a)] on a 50-50 ratio by weight. Silver serves as a binder as well as an electrical conductor. As a general rule, the amount of silver is kept as small as feasible for good pressing, particularly for samples of high molecular or atomic weight. The mixture of sample and silver is blended for at least 30 minutes on a standard Wig-L-Bug.

Radial or Unilateral Pressing

True isostatic pressing has one major fault in that some materials seem to "poker chip" when pressed isostatically; ie, the rod separates into small wafers when removed from the mold. For this reason, the laboratory has adopted the second method which is termed "radial or unilateral pressing".

In radial or unilateral pressing, the naphthalene mold is prepared in a die, as can be seen in Figure 6. The plastic portion of the die is made from an epoxy (871 + 828 resin in a 50-50 mix with triethyltetramine as a curing agent); the metal rods and end caps are of stainless steel. After the mold is prepared, it is removed from the

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(a) Silver powder of 99.999 percent purity obtained from Cominco, American, Inc, 818 W. Riverside Avenue, Spokane, Washington 99201.

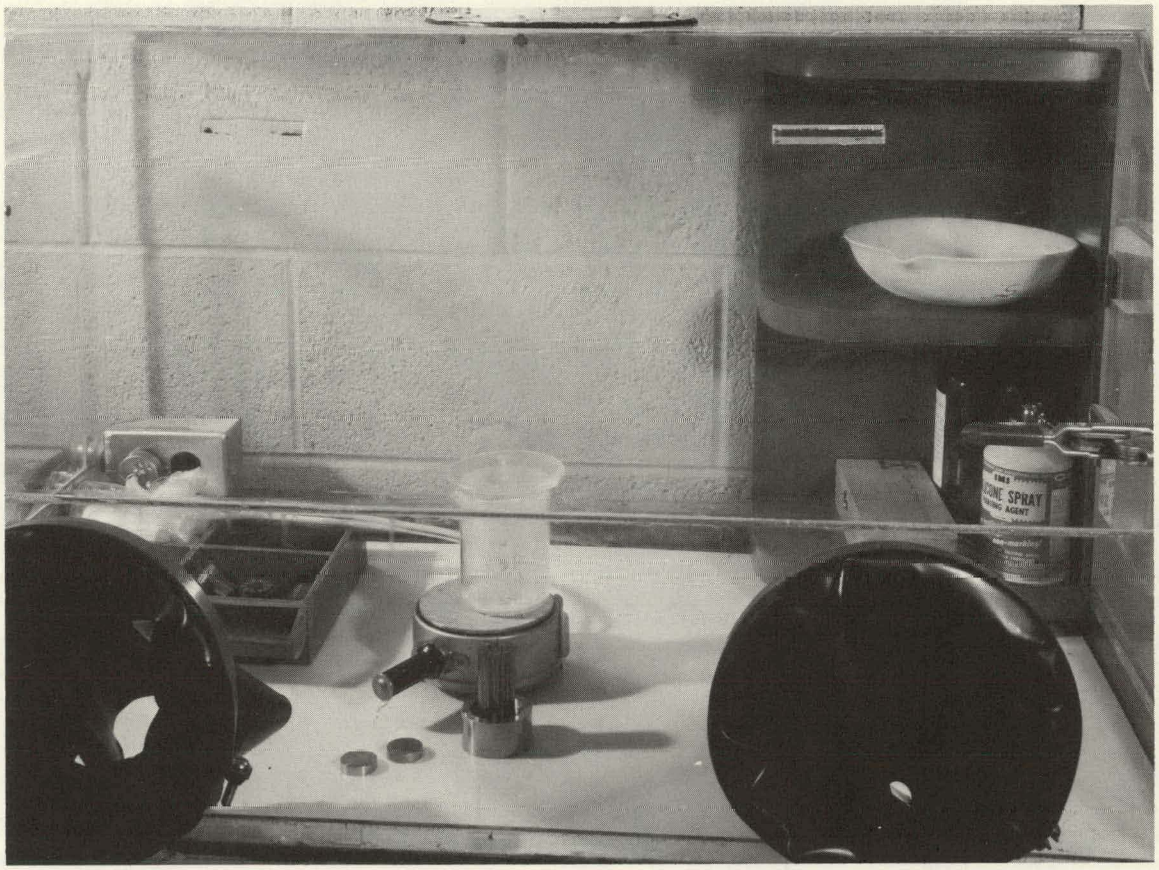

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Figure 5. EQUIPMENT USED FOR MOLD PREPARATION.

die and one end cap sealed with tape. The sample or sample-silver mixture is then poured into the center of the naphthalene mold, packed firmly in place by tapping, and the other end cap sealed. Small punctures are made through the tape at the mold-cap connection to speed up pressure equilibrium. Finally, the mold assembly is placed in a fingercot and evacuated. Failure to evacuate would cause the fingercot to rupture under pressure thus exposing the sample powder to oil. The sample powder must remain dry and free from oil. A sample that has been wet with oil will not yield a usable rod.

After the assembly is evacuated and the fingercot properly sealed, the sample is pressed at pressures between 30,000 and 180,000 psi. (The most commonly used pressure is ~ 100,000 psi.) After pressing, the naphthalene mold is removed from the die in a clean environment, and the naphthalene removed by dissolution in acetone or by sublimation in warm air. Figure 7 is a view of an assembled die, naphthalene mold, and end caps. Figure 8 shows various pressure vessels used in this high-pressure pressing. The one used for sample pressing is in the center. The press is quite similar to the small press pictured in Figure 3.

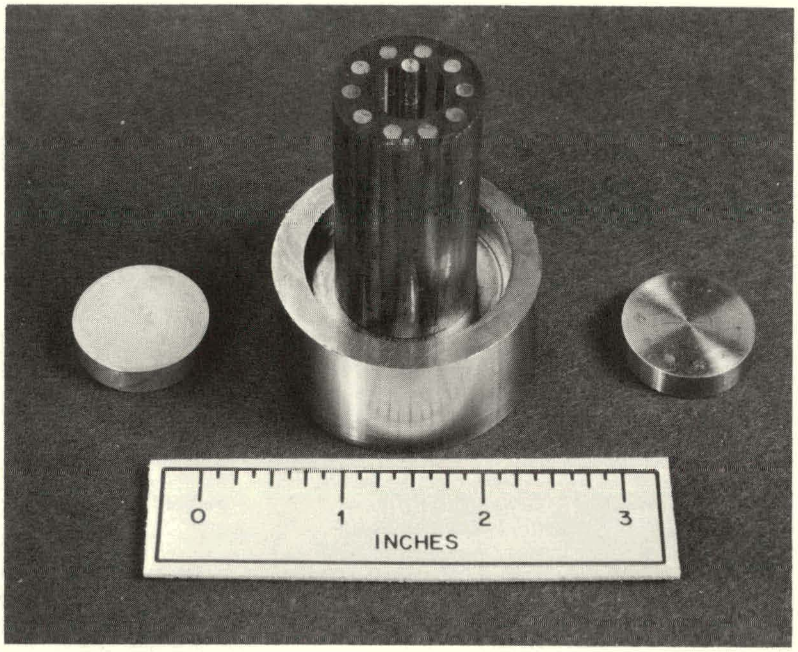

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Figure 6. DIE ASSEMBLY FOR RADIAL OR UNILATERIAL PRESSING.

Figure 9 shows an aluminum rod that was pressed in this manner, then broken into two electrodes and sparked. Note the nail-like head of the section on the right. Such a head is characteristic of rods pressed in this mold.

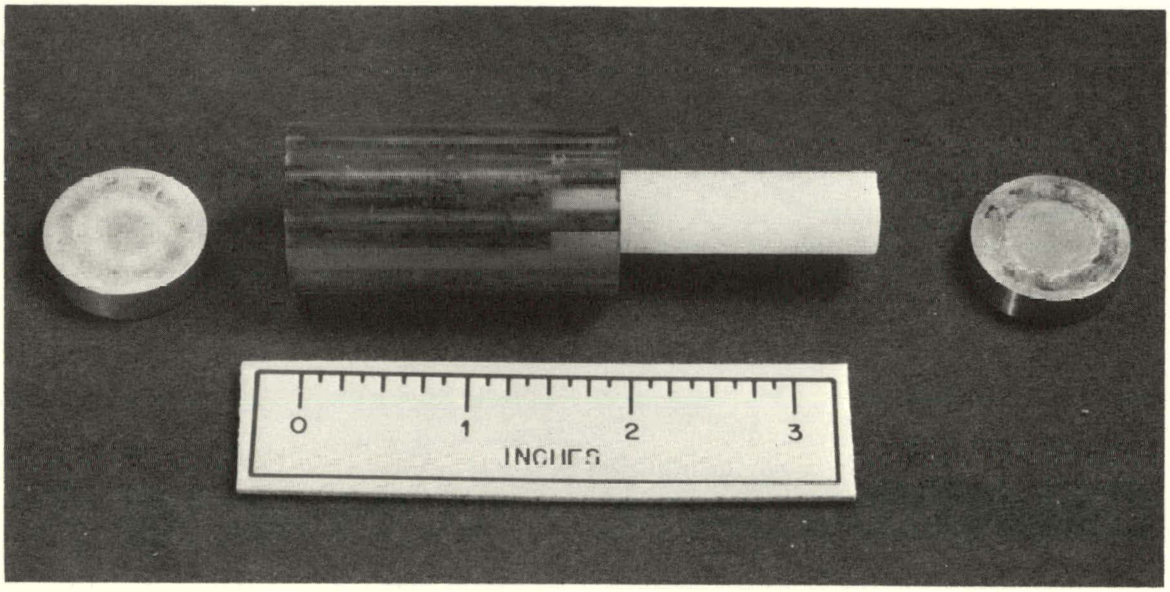

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Figure 7. RADIAL OR UNILATERAL NAPHTHALENE MOLD, DIE, AND END CAPS.

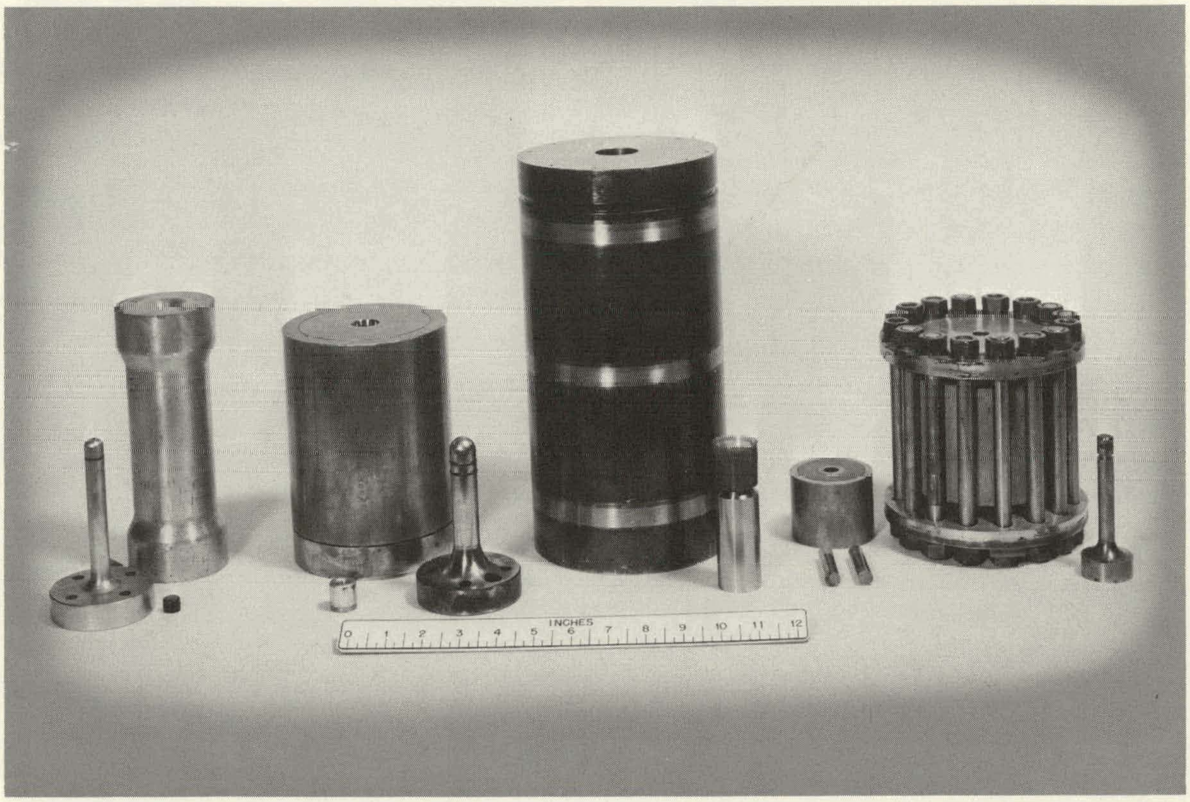

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Figure 8. SEVERAL TYPES OF PRESSURE VESSELS.

DISCUSSION

For true isostatic pressing, the material to be pressed is contained in a mold made of some material that becomes liquid at high pressures. The mold is so arranged that the pressure of the fluid medium is translated to the sample in all directions.

In radial pressing, the sample is also contained in a mold made of a material that becomes a liquid at high pressures; however, the two ends of the mold are held rigid by supports so that no pressure is exerted on the sample parallel to its longitudinal axis. All pressure is exerted around the circumference of the cylindrical mold; ie, perpendicular to the longitudinal axis.

Naphthalene has been used as a mold material for the following reasons: (1) becomes a liquid at pressures above 5,000 psi; (2) when the pressure is released and the naphthalene returns to the solid state, there is little or no spring back; (3) naphthalene is relatively inexpensive and available in high purity; (4) the final mold is easily removed from the pressed rod either by sublimation or dissolution.

The methods of pressing described herein have been used to prepare over 1,000 sample electrodes.

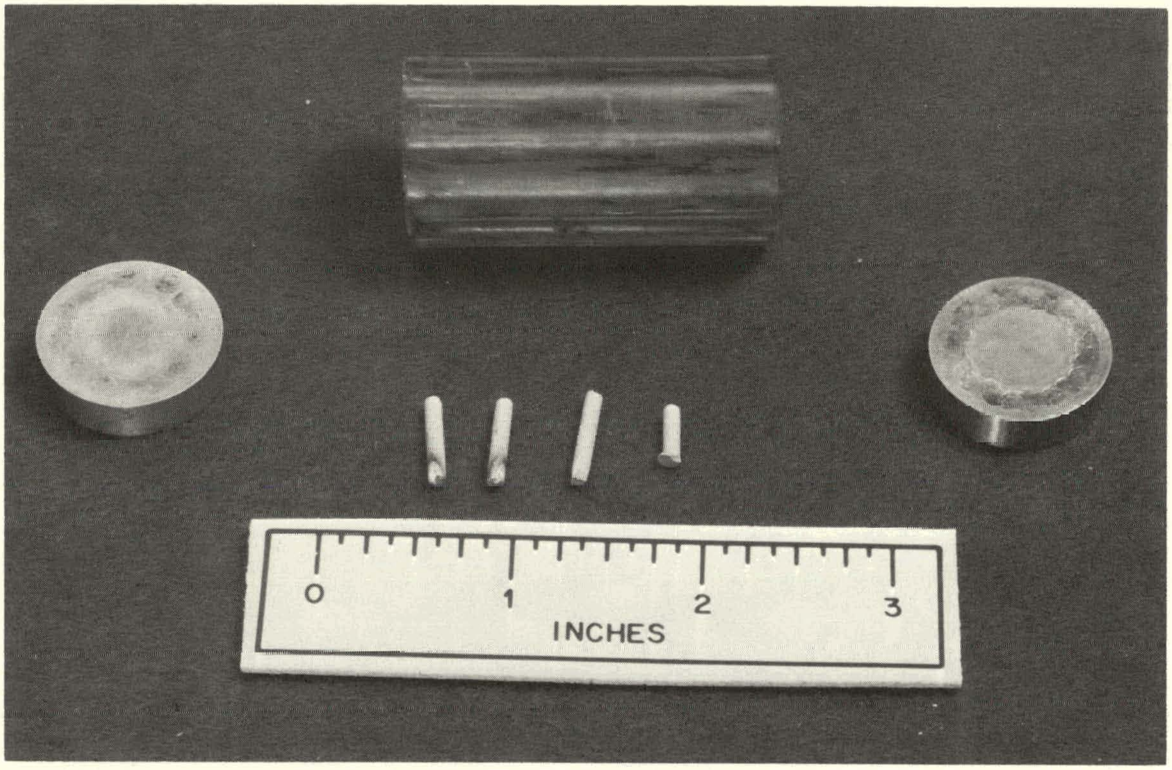

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Figure 9. AN ALUMINUM ROD PRESSED BY ISOSTATIC PRESSING.

Table 1 presents a list of the elements and compounds that have been pressed by these methods. In the list, no distinction has been made between those materials that require silver and those that do not.

The method is reasonably reliable although a small percentage of the samples have not yielded a satisfactory rod on the first pressing attempt. Most of the failures occurred with the true isostatic method and were, in the majority of cases, due to the formation of "poker chips" by the sample rods. It has been observed that if the samples are held at the high pressure for three to five minutes, better-quality rods are formed.

Several factors must be considered in preparing powders for analysis if a representative analysis is to be obtained. Perhaps the most important consideration is avoiding the addition of contaminants during the mixing, loading, and pressing steps. If a contaminant is added to a sample in particulate form, it is possible for as little as one microgram of a contaminant to appear as several parts per million of impurity. This result is due, primarily, to the small volume (0.25 to 0.01 cc) sampled by the spark.

Table 2 lists eight elements known to be present in the silver powder used in pressing powder samples. The column at the right gives the range of each known impurity detected in rods fabricated from the commercially supplied silver powder.

Table 1

MATERIALS PRESSED BY ISOSTATIC PRESSING

Elements	Compounds	
Aluminum	Aluminum Oxide	Tantalum Oxide
Antimony	Beryllium Oxide	Thorium Oxide
Arsenic	Boron Carbide	Titanium Carbide
Beryllium	Boron Nitride	Titanium Oxide
Boron	Calcium Fluoride	Uranium Dioxide
Cadmium	Cobalt Oxide	Uranium Octoxide
Carbon	Iron Oxide	Uranium Trioxide
Diamond	Lithium Carbonate	Yttrium Oxide
Graphite	Lithium Chloride	Zirconium Chloride
Chromium	Lithium Fluoride	Zirconium Oxide
Cobalt	Lithium Hydride	Miscellaneous Materials
Copper	Lithium Hydroxide	Basalt
Gold	Lithium Oxide	Bones
Iodine	Magnesium Oxide	Dirt
Iron	Molybdenum Oxide	Fecal Matter
Lead	Nickel Oxide	Flesh
Manganese	Niobium Oxide	Granite
Molybdenum	Potassium Chloride	Grass
Nickel	Scandium Oxide	Limestone
Niobium	Silicon Oxide	Ores
Silver	Sodium Chloride	Rare Earth Oxides
Sulfur	Sodium Fluoride	*Residue from Plastics Ignition*
Tantalum	Strontium Oxide	Urine Residues
Tin		
Titanium		
Tungsten		
Uranium		
Vanadium		
Zinc		

In order to evaluate the pressing for each batch of samples, one or more silver rods are prepared and analyzed at the same time as the samples. This method provides a monitor of the pressing method as well as providing values for the impurities in the *silver which are used to correct concentrations of impurities detected in the sample.*

From the data in Table 2 it is indicated that, under optimum conditions, no more than 1 to 2 ppm of iron and silicon should be added to the samples during pressing.

There are at least two methods of treatment that may be applied to the analysis of nonconducting materials by spark-source mass spectrography. One method may be identified by the term "probe analysis"(2) in which a nonconducting crystal or compact

Table 2

IMPURITIES PRESENT IN SILVER POWDER

Element	Known Concentration (ppm)	Concentration in Pressed Rod (ppm)
Aluminum	0.1	0.15+
Calcium	5	3 - 7
Copper	0.1	0.3 - 0.5
Iron	0.1	0.4 - 1.5
Lead	0.1	0.15 - 0.4
Magnesium	2	1 - 2
Silicon	0.5	2
Tin	3.0	1.5 - 2.5

is sparked with a counter electrode of gold or tantalum. Powders may also be analyzed by dissolving the sample, evaporating the solution on support electrodes, and then analyzing the residue, called "solution analysis".(3,4)

Both of these methods have characteristics that leave something to be desired. In the "probe" method, the spectrum may include contributions from the probe electrode that vary considerably from one sample to the next. Consequently, determination of the probe contribution to the spectrum is not readily obtainable. However, this method is quick and convenient and is especially useful for single-crystal nonconducting samples.

Many problems present themselves in using the "solution" method. Quite frequently there is the problem of dissolving the sample, which is difficult for some matrices. In addition, it is necessary to have available blanks for the acids and other reagents used to dissolve the samples. It also may be necessary to determine the contribution to the spectrum from such items of equipment as beakers and spatulas that are used to handle the samples.

To obtain a usable sample rod from a nonconducting sample, the following requirements must be met: (1) the electrodes must be electrically conducting; (2) the physical strength must be sufficient to allow the samples to be held in the ion source; (3) the support medium should provide a minimum of interference in the spectrum; (4) the support material must be of high purity and any impurities present must be accurately known; (5) for quantitative analysis, any contribution of the support material to the spectrum should be constant.

In pressing powders, most laboratories use graphite as the support medium.(5) However, the choice of silver rather than graphite at Y-12 is based on several considerations:

1. The mass spectrograph detects concentrations of ions rather than grams of the material; and, even though both materials will conduct the electric current when pressed with nonconducting powders, a 50-50 weight mixture of sample and graphite (a low-atomic-weight material) may be considerably less than 50-50 on an ion basis, while for a 50-50 weight mixture of sample and silver (a high-atomic-weight material), as much as 80 percent of the atoms may be sample rather than support material. This sharp contrast is clearly indicated by the data presented in Table 3.

Table 3

CONTRAST BETWEEN WEIGHT AND ATOM COMPOSITION OF A ROD MADE OF SILICON AND A SUPPORT MEDIUM

Material	Weight Composition (%)	Atom Composition (%)
Graphite	50	70.07
Silicon	50	29.93
Silver	50	20.66
Silicon	50	79.34

2. In order to obtain equivalent atom detection limits in a graphite-supported electrode, an exposure 2.6 times as great as that for silver is required. Of course, both types of rod must be corrected for support impurity contributions and for dilution of the sample by the support material.

3. Possible interferences in the mass spectrum must be considered since spark-source mass spectrographs produce species that are highly abundant, multiply charged, and polyatomic. Carbon produces the $^{12}C^{+2}$ and $^{12}C^{+3}$ ions which would interfere only on $^{6}Li^{+}$, $^{4}He^{+}$, $^{2}H_2^{+}$; however, the element also produces $^{12}C_N^{+}$ $^{12}C_N$ $^{13}C_M$ polymers plus $C_NH_X^{+}$ ions. These polymers have been observed at least as far up the spectrum as C_{22}^{+} (M/e 264). Because of the mass defects, a resolution of 1,600 is required to resolve C_2^{+} from $^{24}Mg^{+}$ and a resolution of 920 to resolve C_4^{+} from $^{48}Ti^{+}$. A mass spectrograph usually exhibits such resolution but not always with very dense lines. In addition, the carbon spectrum consists of at least four lines, one mass unit apart, spaced every 12 mass units across the photographic plate. This line concentration increases the complexity of the sample spectrum and the probability of erroneous interpretation as to the origin of the spectrum lines.

4. When combined with a sample matrix, the graphite support produces MC, MC_2^{+}, M_2C^{+} ions and carbonyl molecules with the sample, M, which further complicate the spectrum. On the other hand, silver produces only one polymer ion that is detected on a normal mass-range plate which occurs as three lines at $^{107}Ag_2^{+}$,

^{107}Ag $^{109}Ag^+$, $^{109}Ag_2{}^+$. Silver also forms polycharged species ^{+1}Ag through ^{+6}Ag; but, because of the odd mass of the silver isotopes, these polycharged species do not obstruct any mass at lower mass levels and, therefore, interfere in no way with the interpretation of the plate. The silver does not form compound ions as readily as does the carbon so that only a small amount of $AgCl^+$ ions and usually $AgOH^+$ are detected, and MAg^+ where M is the matrix sample ion. In addition, the secondary fog found on the plate is much higher with a graphite rod than with a silver rod.

On the basis of these considerations, high-purity silver metal has been selected as the support material for pressing nonconducting powder samples. Gold and bismuth would also be acceptable; however, the gold does not press as well as silver, and not enough bismuth has been conveniently available with sufficient purity.

The method of radial or unilateral pressing has been adopted almost exclusively at Y-12. True isostatic pressing is still used occasionally, but true isostatic pressing yields an acceptable rod only about 95 percent of the time while the unilateral pressing method is effective about 98 percent of the time. One disadvantage of the two methods is that 45 to 60 minutes are required to prepare, load, and press the powder samples.

In conclusion, a method of pressing powder samples for spark-source mass spectrographic analysis has been devised that is reliable in producing satisfactory sample rods which are free from contamination due to handling and pressing. Presently, an alternate method is being investigated that will reduce the preparation time.

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