SECONDARY-SOURCE ENERGY-DISPERSIVE X-RAY SPECTROMETER

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A secondary-source energy-dispersive x-ray spectrometer has been built and tested. In this instrument the primary source of x rays is a tungsten-target tube powered by a high-voltage (75 kV), a high-power (3.7 kW) generator from a wavelength spectrometer (G.E. XRD-6). The primary polychromatic x rays irradiate an elemental foil, the secondary source. Its characteristic essentially monochromatic x rays are used to irradiate the sample. Fluorescent x rays from the sample are detected and resolved by a lithium-drifted silicon detector, multichannel-analyzer system. The design of the instrument provides a convenient means for changing the secondary, and hence, the energy of the excitation radiation.

In most commercially available x-ray spectrometers excitation is accomplished by irradiating the sample directly with a low-power tube. As a result, the whole spectrum is cluttered with white radiation from the tube scattered by the sample into the detector. With monochromatic excitation the scattered radiation is outside the energy region of interest, the signal-to-noise ratio is hence quite superior, and the detection limit for most elements is markedly lower.

Our instrument is also superior to the commercial secondary-source instruments in that the determination of a larger number of elements can be based on the measurement of the K x rays. With an x-ray tube operating at 75 kV, a secondary source having an atomic number as high as 67 (holmium) can be used, permitting determination with K x rays of such elements as iodine, cesium, barium, and the light rare earths. For instruments operating at $\leq$ 50 kV, determination of these elements must be based on the L x rays. Because these L x rays are readily absorbed by the sample matrix, the composition of the matrix must be stringently controlled. Also, since these L x rays are in the same energy range as the K x rays of such common elements as potassium, calcium, and titanium, determinations based on the L x rays are more subject to interference.

A cross section of the spectrometer along the optical path is shown in Figure 1. The housing, which is fabricated from steel pipe, consists of two chambers, one for the tube which has a 5/8" wall, and one for the sample changer, which has a 3/8" wall. The design reflects an attempt to minimize both the amount of scattered radiation within the instrument and the length of the optical path. The instrument can be operated in air or under vacuum.

The secondary sources are periscope shaped and have 2- × 2-in openings at both the upper and lower ends (A and B in Figure 1). The copper, molybdenum, and silver sources are fabricated from 10-mil metal sheet stock. The tellurium, samarium, and holmium sources are made by covering over the sloped face (C) of a copper source with a 2- × 3-in piece of these metals. As these sources are used only for the determination of elements having atomic numbers greater than 40, the copper x rays that impinge on the sample and are scattered into the detector can be absorbed by interposing a thin sheet of aluminum between the sample and the detector. A port in the upper chamber permits manual changing of the secondary sources.

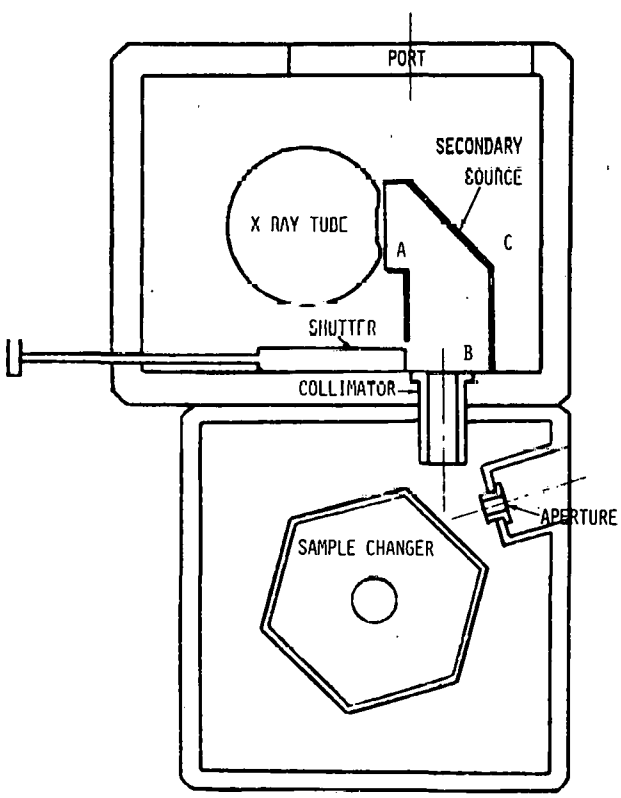

FIG. 1.--Cross sectional view (along the optical path) of the x-ray spectrometer.

The cylindrical collimators and apertures are made from high purity copper or cadmium. The copper set is used in determinations of elements with atomic numbers in the range 40 to 65; the cadmium set is used for elements with atomic numbers less than 40 or greater than 65.

The hexagonal sample holder is made from 1/8-in thick Lucite sheet and is mounted on the end of a steel rod which penetrates the back face of the sample chamber. This holder permits the analysis of up to six samples without opening the spectrometer. Samples are mounted through a port in the front face of the sample chamber. This port is interlocked electrically with the shutter; it cannot be opened when the shutter is in the open position without interrupting power to the x-ray tube.

A novel method has been developed to package and mount both powder and liquid samples for presentation to the spectrometer. The packages are prepared by bonding 1.5-mil Mylar laminated film (0.5-mil Mylar bonded to 1.0-mil polyethylene) to the outer face of a 2- × 2-in cardboard slide mount. The sample is then placed on the film in the center of one frame, the mount folded, and a film-to-film seal made around the sample. Liquid samples of up to 250 μl are contained in a dimple impressed in the center of one frame and sealed as above.

The detection limit for elements having atomic numbers from about 20 (calcium) to 48 is in the range of 10 to 40 ng. These values are the amounts of the individual elements which, when mounted between two sheets of 1.5-mil Mylar and assayed for 1000 sec, would produce a signal that is twice the standard deviation of the background. For the elements which have atomic numbers in the range 48 to 65, the detection limit is about 200 ng if the analysis is based on the measurement of their K x rays. This decrease in sensitivity is due to the fact that the intensity of x rays that can be obtained from a secondary source with a relatively high atomic number, e.g., holmium (67), is much lower than that from secondary sources such as molybdenum (42) and silver (47). However, a detection sensitivity for these elements of about 40 ng can be obtained if the analysis is based on measurement of the L x rays. The disadvantages of this are: (1) there is high mass absorption due to the relatively

low energies of these x rays and (2) resolution of the several peaks from each element is incomplete. The latter disadvantage is particulary pronounced for those elements at the low end of this range, e.g., cadmium.

At present the reproducibility of measurements made with this instrument is about 5%. This variation is due primarily to a problem of positioning the mount in the slots on the sample changer. The errors due to such other factors as the reproducibility with which a particular position of the sample changer can be made and the geometric equivalency of the six positions on the sample changer were shown to be negligible. Thus it appears that the reproducibility can be improved by designing a system for holding the sample mounts which eliminates their movement on the sample changer.

The reported reproducibility was achieved by normalizing integrated photopeak intensities to the integrated intensity of the backscattered exciting radiation. Even greater precision will, of course, result from incorporating an internal standard in the sample.