is wasteful; all detectable chemical species can be photographed at the same time by the use of multiple display oscilloscopes. Alternatively the pulse height information could be recorded for later analysis, perhaps digitally, with the possibility of improving the picture quality through application of image-enhancement techniques.

An interesting possibility is to form a demagnified image of the pinhole, with the use of reflection optics, and scan the sample through the focus. This would provide greater resolution without a loss in counting rate, in contrast to the present inverse-square trade-off.

By operating the synchrotron at higher energy, thicker samples and higher atomic numbers could be examined. The same result can be achieved more efficiently by the installation of a high-field magnetic "undulator" (a magnet with a row of pole pieces for producing a spatially alternating field) in a synchrotron straight section, thus increasing the intensity of the synchrotron radiation and extending its spectrum to higher energies. A gain in counting rate, hence improved sensitivity, would also result.

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Mercury Detection by Means of Thin Gold Films

Abstract. *The adsorption of elemental mercury vapor on a thin (several hundred angstroms) gold film produces resistance changes in the film. An instrument for the detection of mercury based on this phenomenon is simple and rapid and requires no chemical separations other than passage of the vapor sample through a few standard dry filters. The instrument is portable, and the technique is directly applicable to environmental problems and geochemical prospecting. The limit of detection of the prototype instrument is 0.05 nanogram of mercury.*

In recent years much attention has been devoted to the development of methods for the detection of low concentrations of Hg, both for environmental studies and for geochemical prospecting. A portable instrument capable of rapid, inexpensive analysis is desirable for these purposes. Most semiportable devices for the detection of low concentrations of Hg have relied on the atomic absorption technique. A variety of modifications have been described, all based on the fact that Hg absorbs at 2537 Å (*1, 2*). A serious limitation, however, is the presence of interfering substances such as H_2O, O_3, SO_2, and a variety of organic compounds and fine particulates (*2*). These absorb or scatter electromagnetic energy in the spectral region of interest. As a result of the efforts made to overcome these interferences, the resulting instruments have lost either their portability or their sensitivity, or both.

We have developed an extremely sensitive and portable Hg detector (*3*) based on the phenomenon that a thin Au film undergoes a significant increase in resistance upon the adsorption of Hg vapor. This resistance change is linear in nanogram concentrations.

Gold films are prepared by vacuum evaporation on ceramic or glass substrates in a conventional high-vacuum system (10^{-6} torr) with the use of a Cr underlayer and no substrate heating. After preparation, the films are annealed in the atmosphere at 150°C. Problems are encountered at higher annealing temperatures (*4*). The film resistances range from 300 to 1500 ohms. Their thicknesses vary between 400 and 75 Å, with sheet resistivities of 2 to 10 ohms per square, respectively.

A diagram of the instrument is shown in Fig. 1. Two films of equal resistance are used, one as a sensor and the other as a reference. They are contained within a Plexiglas chamber designed to allow a constant flow of carrier gas to pass over the films. The films are connected into opposite arms of a simple d-c bridge circuit and balanced.

The Au films extract Hg from a carrier gas, normally air filtered through activated charcoal. There are two ways that the sample can be introduced into the carrier gas. If the sample is a solid, for example, a biological sample or a soil, it is decomposed and the Hg is concentrated on a noble metal collector. This Hg, in turn, is liberated in the furnace (*A* in Fig. 1) and then surged into the flow path of the instrument. If the sample is already a vapor, it is injected with a syringe through a rubber septum (*B* in Fig. 1). This method of introduction can be modified to permit continuous sampling, thereby bypassing the hypodermic introduction.

Before the carrier gas enters the film chamber, the gas is scrubbed of H_2O vapor and acid vapors such as H_2S in a filter train containing $MgClO_4$ and Ascarite. The airstream is then divided into two fractions. One fraction is scrubbed of Hg by passage over $PdCl_2$ (*5*) before it enters the reference chamber. The other fraction is passed over the sensing film. Changes in the resistance of the sensing film are due to Hg adsorption, and variations in the film resistance due to thermal fluctuations or other adsorbing gases are neutralized.

Two factors which affect the sensitivity of the instrument are film thick-

Table 1. Precision data for the Au-film Hg detector; S.D., standard deviation.

Hg vapor standard	Amount of Hg		S.D. (ng)	S.D. (%)	99% tolerance interval (ng)	Determinations (No.)
	Mean (ng)	Range (ng)				
1	0.5	0.47– 0.53	0.03	6	0.09	17
2	1.1	1.05– 1.17	.04	4	.12	16
3	2.2	2.1 – 2.3	.07	3	.21	16
4	3	2.8 – 3.2	.13	4	.39	16
5	11	10.2 –12.0	.62	6	1.9	15
6	25	21.1 –29.2	2.6	10	8.0	15

ness and carrier gas flow rates. For a given quantity of adsorbed Hg the fractional resistance increase is greater for thinner films. Variations in flow rates affect the contact of the vapor with the collecting film. The chamber housing the sensor and reference films is designed to assure a turbulent flow of the vapor sample, thereby affording maximum contact with the Au film surface. At a given flow rate the amount of Hg collected from the vapor sample is constant, reaching 85 percent efficiency at a rate of 200 ml/min. The response time of the instrument is also dependent on the flow rate. However, the resistance change of the sensing film resulting from Hg adsorption is essentially instantaneous.

On the prototype instrument 1 ng of Hg produces a fractional change in resistance of 4×10^{-5} in a sensing film of area 2.5 cm^2, with a signal-to-noise ratio of 20 : 1. Detection of 5×10^{-11} g of elemental Hg is possible. The reproducibility, measured on standard samples, is shown in Table 1. We find a 99 percent tolerance interval of less than ± 20 percent of the amount of Hg present over a range of less than 1 ng to 10 ng or more. As can be seen from the percent standard deviations, problems arise at very low concentrations because of electronic noise, as well as the difficulty of reproducibly introducing standard quantities of Hg. At high concentrations the films saturate with Hg, and this saturation reduces the precision. It is possible to correct for this saturation with a calibration curve. When this was done for the 25-ng samples, the scatter was reduced appreciably.

The present film design produces a linear change in resistance for amounts of Hg ranging from 5×10^{-11} to 1×10^{-7} g. Larger amounts of Hg produce nonlinear responses, because of the saturation of the Au surface. Although this is a serious limitation, it may be overcome to a certain degree by the development of sensing units with an increase in available Au surface or by dilution of the incoming gas stream. When the films approach nonlinearity, they may be heated at 150°C for 10 minutes. This heating removes the adsorbed Hg, thereby cleaning the film and restoring its former sensitivity.

In exploratory experiments we have investigated the applicability of the instrument for measuring other gases. The results vary. The instrument is at least as sensitive to H_2S as it is to Hg, and so can potentially serve as an H_2S detector. Other gases tested, SO_2, CH_4, and CO, show minimal response.

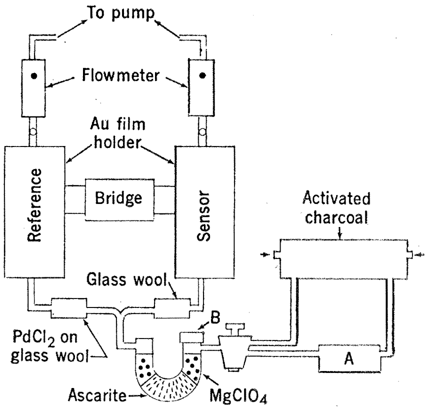

Fig. 1. Block diagram illustrating the flow path of the instrument.

The success of the Au-film Hg detector depends primarily on two phenomena: (i) the selective adsorption of Hg atoms on the Au film, and (ii) the large increase in the scattering of conduction electrons at the Au surface resulting from the adsorbed Hg atoms.

The high sticking coefficient for Hg atoms on Au has been known for a long time. Huber (*6*) showed that the work function of Au had long been in error because of a tightly bound layer of Hg on the Au surface. In the present configuration, where the Au is exposed to the atmosphere, the continued large collection efficiency implies either that Au has not adsorbed appreciable O_2, H_2O vapor, or other gases, or that the Hg atoms are able to almost instantaneously penetrate loosely sorbed material on the Au surface.

The effects of adsorbed Hg atoms on the conductivity of the Au films is a surface rather than a bulk alloy effect. The magnitude of the resistance change for a 300-Å film is about one-third as much as the resistance change for a bulk alloy containing the same amount of Hg. In addition, the effect occurs instantaneously, rather than with a time constant appropriate for the diffusion of Hg into the Au film.

The resistance increase resulting from a partial Hg overlayer on the Au is produced by the change in the scattering of the conduction electrons when they hit the surface (*7*). An alternative explanation, that a resistance increase arises from a decrease in the number of conduction electrons, is not acceptable because of the very strong screening of the foreign atom that is provided by the degenerate Fermi gas of electrons (*7*).

In several experiments there have been large increases in the resistance of specular Au films upon the addition of very thin overlayers of either Au (*8*) or other materials (*9*). The magnitudes of these increases are comparable to the increases we see in the adsorption of Hg. Two rather similar models have been used to explain these experiments, and either model is apparently applicable to our results. Lucas (*10*) constructed a model in which he considers the overlayer as a thin layer having a much shorter mean free path than the original Au film. In the model of Mitchinson and Pringle (*11*) the overlayer is considered as being made up of separate islands with the surface of each island assumed to have complete diffuse scattering.

In the present experiments, although no special efforts were made to ensure that the Au films were specular, it is reasonable to assume a similar explanation to that described above for the observed resistance increases. It is assumed that there are microregions where the conduction electrons are specularly reflected before the adsorption of Hg, and these regions are sensitive to the change from specular to diffuse scattering which is caused by the adsorbed Hg.

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