Tellurium: A New Sensitive Test

Abstract. *A new, extremely sensitive method for the quantitative determination of tellurium is based on the induced precipitation of elemental gold from a 6*N *HCl solution containing gold chloride, cupric chloride, and hypophosphorous acid; the amount of gold reduced is proportional to the amount of tellurium present. As little as 1 nanogram* (1×10^{-9} *g) of tellurium gives a measurable reaction with 1 mg of gold in 50 ml of solution.*

In a study of reactions suitable for the isolation and determination of traces of tellurium in geologic materials, we (*1*) determined conditions for the quantitative reduction and precipitation of a few micrograms of tellurium as elemental tellurium from complex solutions by using hypophosphorous acid and adding gold as a collector. When the Te and added $AuCl_3$ were reduced at ambient temperatures, the amount of gold reduced and precipitated as elemental Au appeared to be proportional to the amount of Te present. The reaction provided a test for Te 1000 times more sensitive than any known method (*2*); as little as 1 ng (1×10^{-9} g) of tellurium reacts measurably with 1 mg of gold in 50 ml of solution.

The conditions for the test are: to 50 ml of 6*N* HCl at 15°C are added, successively, accompanied by thorough mixing, 1 mg of gold as $AuCl_3$ (1 g Au in 100 ml 6*N* HCl), 6 mg of copper as $CuCl_2$ (3 g $CuCl_2$ in 100 ml 6*N* HCl), 1 ml of solution containing the sample dissolved in concentrated sulfuric acid, and finally 1 ml of 50 percent hypophosphorous acid (H_3PO_2). At a fixed time after the addition of the hypophosphorous acid, the solution is filtered through a Millipore filter (0.45 μ pore size). The gold so collected is dissolved by washing the filter with HBr containing a small amount of free or elemental bromine and the amount of gold is determined by a modification of the rhodamine-B colorimetric procedure (*3*). Alternatively, the amount of Te can be estimated by comparing the turbidity of the sample with that of standards or by comparing the color intensity of the spots obtained after filtration.

The rate of the reduction of gold chloride from a 6*N* HCl solution by hypophosphorous acid is governed not only by the amount of Te but also by the concentrations of the Au, Cu, and H_3PO_2, as well as the temperature of the solution.

Solutions of $AuCl_3$ and $CuCl_2$ can be prepared with commercially available reagents. However, commercial hypophosphorous acid often varies in strength and purity (*4, 5*). The correct amount giving the reaction we describe was determined experimentally: 1 ml of 50 percent crystalline hypophosphorous acid prepared by the procedure of Jenkins and Jones (*5*).

If the concentration of Au, Cu, and H_3PO_2 is adjusted, when no Te is present, so that about 0.5 percent of the Au is reduced and precipitated in 1 hour at the selected temperature, then 1 ng of Te will produce a marked increase in the percentage of the Au reduced.

The relationship of the amount of gold precipitated in 5 minutes to the amount of tellurium present and the reproducibility of this precipitation is shown in the calibration curve (Fig. 1). The curve is based on the photometric measurement at 335 mμ in a 1-cm cell of the absorbance of the rhodamine-B complex formed with the gold.

Arsenic, selenium, mercury, and antimony also induce the precipitation of elemental Au, but much larger amounts of these elements are required. Bromides and iodides interfere by reducing the sensitivity of the reaction. All these interferences may be removed by evaporation of the sample, with sulfuric and hydrobromic acids.

Hydrobromic and sulfuric acid solutions containing 1000 μg of arsenic, selenium, mercury, or antimony were evaporated until sulfuric acid fumed; no precipitation of gold was obtained from the remaining sulfuric acid. Similar experiments with Te^{129} as a radioactive tracer indicate that tellurium is not lost by this evaporation.

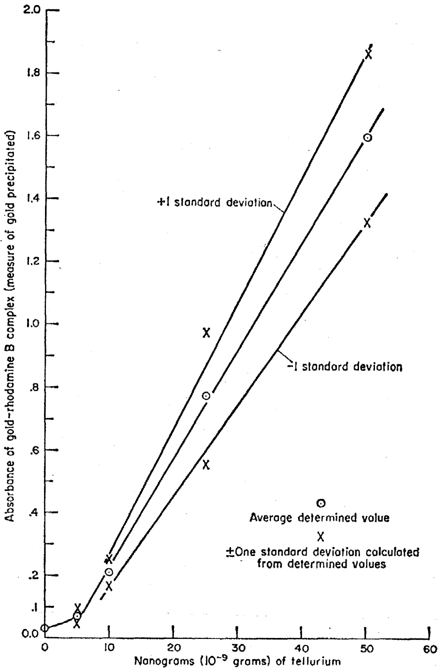

Fig. 1. Gold-rhodamine B calibration curve. Each point represents the average of 14 values for the blank, 9 values for 5 ng, 8 values for 10 ng, and 11 values for both 25 and 50 ng of tellurium.

The following compounds did not interfere with the test in the amounts given when they were added to the usual 50 ml of 6*N* HCl containing Cu, Au, and H_3PO_2: 100 mg of $NaNO_3$; 60 mg of K_2SO_4 and of $Na_2HPO_4 \cdot 7H_2O$; 50 mg of $FeNH_4(SO_4)_2 \cdot 12H_2O$; 30 mg each of $CrCl_3$ and $MgCl_2 \cdot 6H_2O$; 20 mg each of $Al_2SO_4 \cdot 12H_2O$, $BaCl_2$, $Bi(NO_3)_3 \cdot 3H_2O$, $CdCl_2 \cdot 2\frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$, $CaCl_2 \cdot 6H_2O$, LiCl, $MnSO_4 \cdot H_2O$, $NiSO_4 \cdot 6H_2O$, NaF, $SrNO_3$, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, $UO_2(NO_3)_2 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, $Na_2B_4O_7 \cdot 10H_2O$; and 10 mg each of GeO_2, Sc_2O_3, Tl_2O_3, La_2O_3, Ta_2O_5, Ga_2O_3, In_2O_3, $SnCl_2$, and $AgNO_3$. Not all of these compounds were soluble in 50 ml of 6*N* HCl; in these cases whatever dissolved caused no interference. The following elements in the amounts indicated caused no interference: 100 μg each of Pt, Pd, Re, Be, and W, 200 μg of Nb, 1000 μg of Mo, and 2000 μg of Pb. The maximum amounts of these elements which can be tolerated without interference with the test have not been determined.

The method has been applied to the determination of tellurium in native sulfur, various sulfides, iron oxides, and shales. Solutions of the samples were obtained by well-known methods: sulfur and sulfides by digestion with carbon tetrachloride–bromine mixture and nitric acid, iron oxides by fusion with potassium pyrosulfate, and shales by fusion with a mixture of sodium carbonate and potassium nitrate. After the initial treatment of the sample, 1 ml of sulfuric acid and 2 ml of hydrobromic acid were added, and the resulting solution was evaporated until the white fumes of sulfur trioxide evolved. The addition of 2 ml of HBr and the evaporation were repeated three times, after which the cool sulfuric acid solution of the sample was added to 50 ml of 6*N* HCl containing 1 mg of Au and 6 mg of Cu. One milliliter of 50 percent H_3PO_2 was then added, and the solution was allowed to stand 5 minutes before filtering. The amount of tellurium in the sample was read from the standard curve (Fig. 1) by using the absorbance of the rhodamine-B complex of the precipitated gold.

With a 10-mg sample of native sulfur from Lassen Peak, California (*6*), eight analyses ranged from 0.40 to 0.60 part per million; the median was 0.48 and the average 0.49. Comparison with the bismuthiol II method (*2,7*) was favorable. On native sulfur from Little Sitkin Island, Alaska (*6*), a 10-mg sample, in 16 analyses by the new method, showed from 3.0 to 7.0 parts of Te per million (median, 3.5; mean, 4.2). Six analyses of a 5-g sample by the bismuthiol II method showed 3.7 to 5.0 ppm (median, 4.8; average 4.5).

Although in its present state of development the method is not as precise as desired, its extreme sensitivity permits the determination of Te in a variety of geologic materials and especially in minute samples of pure minerals. The method is rapid, simple, and sufficiently precise to yield useful data for the study of the geochemistry of tellurium.

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References and Notes

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6. We thank R. R. Coats for the sulfur sample from Lassen Peak, and G. L. Snyder for the sample from Little Sitkin Island. Publication authorized by the director, U.S. Geological Survey.
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Thin Membranes of Parlodion

Abstract. *Parlodion membranes 50 to 1000 Å thick have been prepared by deposition of isoamyl acetate solutions on the air-water interface under conditions of controlled evaporation. Capacitance and resistance measurements have established the integrity of large areas of these membranes. The former also provides corroboration of the thickness estimated from the amounts of parlodion deposited.*

In a recent review of the preparation of membranes, Carnell and Cassidy described a method for the preparation of uniform and thin membranes of pyroxylin on glass surfaces (*1*). They also pointed out that Gershfeld (*2*) cast thin membranes (300Å or less) on aqueous surfaces with solutions of parlodion in isoamyl acetate solvent.

We encountered difficulty in obtaining uniformly intact membranes by both techniques. It was very difficult to float thin membranes of parlodian (200 Å or less) off the glass plate by the method of Carnell and Cassidy. There was the additional drawback that we were uncertain about the thickness of the membranes. The casting technique (*2*) proved unsatisfactory without proper precautions (*1*). In our hands, air currents removed the solvent so violently, that most of the aqueous surface was not covered with the membrane. As a result, repeated trials to cast completely intact membranes ended in failure.

We have developed a method for producing uniform membranes of definite thickness. It retains the simplicity of the Gershfeld technique but observes the precaution of the Carnell-Cassidy procedure of controlling solvent evaporation.

A known weight of parlodion (purified pyroxylin, Mallinckrodt), usually not less than 5×10^{-3} g/ml of solution, was dissolved in isoamyl acetate. Stronger solutions could be used to prepare thick membranes. A cell of the type shown in Fig. 1 was used for forming membranes. It had a glass ring (inside diameter, 4.6 cm; height, 1.6 cm), one end of which was closed by a tight-fitting rubber stopper that had been cleaned by boiling with strong alkali, and subsequently with distilled water. A platinized platinum electrode, or one end of a salt bridge, or both, could be introduced into the cell through holes bored in the rubber stopper in order to make electrical measurements. The volume of the cell was about 13 ml.

Since the quality of the membrane was governed by the water used, ordinary distilled water, redistilled with acid permanganate in a two-stage quartz still was always used in the preparation of solutions. The cell was filled to the brim with aqueous solution (for example, 0.1*N* KCl), and the surface was repeatedly swept with a clean rectangular piece of Teflon 0.5 cm thick. The cell was covered by a close-fitting beaker (150 ml) with a pin hole at the top through which a calculated quantity of the solution of parlodion in isoamyl acetate was transferred gently on to the aqueous surface with a Hamilton microsyringe. Interference colors develop and slowly disappear, leaving an intact membrane covering the entire aqueous surface. The thickness was estimated from the known quantity of parlodion deposited in the known surface area. This was confirmed by calculations from the measured capacitance and the known dielectric constant (6.4) of parlodion (*3*).

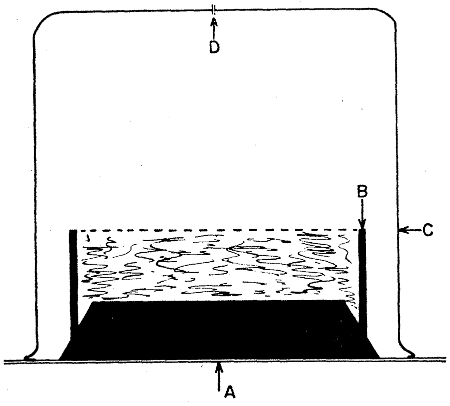

Fig. 1. Assembly for preparation of thin parlodion membranes. *D*, opening in inverted beaker, *C*, through which the fine needle of a Hamilton syringe is inserted to apply a measured parlodion-isoamyl acetate drop on the surface of the solution in glass ring, *B*. *A*, rubber stopper seal for *B*, through which electrodes are inserted.

The integrity of the membranes was checked by measuring both their electrical resistance and capacitance with a General Radio impedence-admittance bridge. A small fluid electrode (0.1*N* KCl in contact with platinized platinum wire, as in the subphase) of $0.28\ \text{cm}^2$ was brought gently into contact with the surface at a number of points in succession so that many determinations of capacitance and resistance were made on each membrane. The order

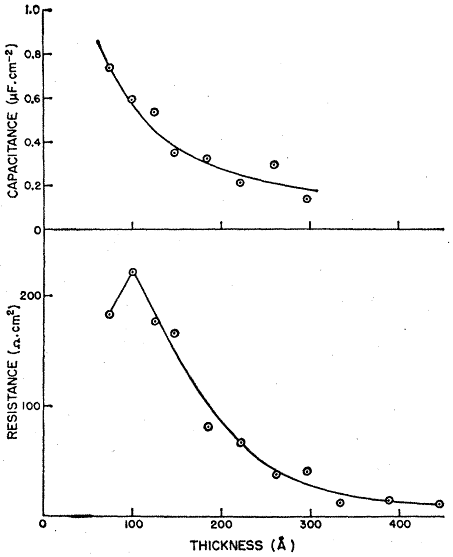

Fig. 2. Typical curves relating membrane resistance and capacitance to the thickness of parlodion membranes.