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POLAROGRAPHIC METHOD FOR THE QUANTITATIVE DETERMINATION OF URANIUM IN ATMOSPHERIC DUST

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DUST COLLECTION

The Instrument

The sample of dust is collected and deposited from a known volume of air using a high voltage electrostatic (Cottrell) precipitator in conjunction with an electric vacuum pump. The instrument was designed and constructed at the Radiation Laboratory of the University of California. Details of construction are outside the scope of this report.

Procedure

The apparatus is set up in the locality to be sampled. Care must be taken that the equipment will not interfere with the normal work in the area. The depositing tube is removed and lined with Whatman No. 42 filter paper. Two rectangular sheets are cut from 18.5 cm circles. One sheet is approximately 12 by 14 cm and the other sheet is approximately 12 by 7 cm. The sheets are made to conform carefully to the circumference of the metal tube in order that no sharp edges will protrude and thus cause sparking. This is accomplished by using small strips of cellulose adhesive tape to fasten the sheet into a cylinder of the proper diameter.

The protector is next attached and the tube replaced. The equipment is now ready for operation; therefore, the high voltage is applied and adjusted if sparking occurs. The motor is started and the by-pass valve adjusted. The by-pass valve was calibrated using a gas flowmeter borrowed from the Physics Department of the University of California. The collector tube was fitted directly to the flowmeter by means of a rubber stopper. An airflow of three cubic feet per minute is always maintained, although this is only an arbitrary value which is chosen to insure a complete deposit of all dust on the filter paper. Glass wool plugs have shown that no noticeable amount of dust escapes through the electrostatic field. Most samples are collected over a period of 24 hours. This usually gives an easily determinable quantity of uranium and also integrates the dust conditions over a greater period of time.

At the end of the test the filter paper is carefully transferred to an Erlenmeyer flask and taken to the laboratory for the chemical treatment and polarographic analysis.

Chemical Preparation

The filter paper and sample are thoroughly wet-ashed with 10–15 ml of conc. H_2SO_4 and then cooled in ice. All organic matter is destroyed by repeated applications of 30% H_2O_2. Extreme care must be exercised to prevent violent action. Only 5–10 ml of H_2O_2 should be added each time to cold H_2SO_4 followed by gentle warming of the resulting mixture. When the organic matter appears to be destroyed, most of the remaining H_2SO_4 is removed by fuming in a stream of air admitted into the flask.

If the sample contains much graphite it should be removed by filtering the sample through No. 40 Whatman paper into a 50 ml beaker, and the filtrate evaporated to near dryness. If any organic coloration remains more 30% H_2O_2 should be added until this coloration disappears. Finally the sample is evaporated and fumed to dryness. In any evaporating operation bumping and boiling can be prevented by directing an air stream on the surface of the liquid.

After all H_2SO_4 is removed 1 ml of 5% H_2SO_4 is added to the sample and the volume adjusted to 6 ml. This gives the proper acidity for the precipitation of copper as the sulfide. Copper should be removed if it is present to any great extent since the half-wave potential of copper lies very close to that of uranium when using 5% H_2SO_4 as the supporting electrolyte. The copper sulfide is removed by filtering through No. 42 Whatman paper wet with H_2S solution and the filtrate evaporated to a volume less than 1 ml. The sample is now ready to be analyzed polarographically.

POLAROGRAPHIC ANALYSIS

The Instrument and Its Manipulation

A Heyrovsky Polarograph Model XI manufactured by E. H. Sargent and Company is available for the analysis of the dust samples. The instrument has been modified by placing a 2000 μf condenser in parallel with the galvanometer. This reduces oscillation due to the time interval between mercury drops. The cell accompanying the instrument has been discarded in favor of a cell constructed by Smith and described in the report Chem S-336 (TEY). The mercury anode and capillary cathode system are borrowed from Dr. Roderick Craig of the University of California Entomology Department.

The cell is washed thoroughly with distilled water and dried by acetone, the last traces of which are removed by a water aspirator pump. The sample is then transferred to the cell and the volume adjusted to 1 ml. Temperature control of the solution is important for accurate analysis. In this work, however, the polarograph is operated at room temperature. The mercury anode is adjusted until the level is just below the side-arm capillary. Oxygen-free nitrogen, saturated with water vapor, is bubbled through the solution for about 10 minutes to remove oxygen from the sample. The nitrogen is made oxygen-free by bubbling it through an NaOH solution of $C_6H_3(OH)_3$.

The pyrogallol solution is prepared by adding a solution of 12 grams of $C_6H_3(OH)_3$ in 40 ml of water to a solution of 60 grams of NaOH in 100 ml of water. Oxygen has a current step which occupies the early section of the polarogram and interferes with the cations up to approximately -1.6 volts.* After all oxygen has been removed the nitrogen is stopped and the stopper surrounding the capillary placed tightly in the cell. The end of the capillary should be approximately 1 cm above the level of the anode.

The mercury head above the capillary is next adjusted to the predetermined height. This height is not critical but it has been shown that both the mercury head and the bore of the capillary must be the same as that used in the standardization for accurate analysis.

To begin a routine operation first turn Select V and Adjust V of the polarograph to the proper Bridge V which is usually 4 volts. This gives a current step steep enough so that eight polarograms are possible on one film and yet not too rapid a potential increase to cause a current lag in the galvanometer. Turn lamp on and adjust the 'zero' point of the galvanometer. This is usually adjusted to 10 on the current scale as this places the tracing at a convenient place on the film.

As soon as preliminary oscillation ceases the motor is turned on and the film shutter opened. Of course the current sensitivity R and the Applied Potential range S must be selected, but once that has been determined it is not usually necessary to change them for each dust sample analysis. Since uranium

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* Value given in Polarographic Analysis by E. H. Sargent and Company.

has a half-wave potential of approximately −0.49 volt the Applied Potential Scale need not go beyond 0.2 which, for a Bridge V of 4 volts, would give a range from 0.0 volt to 0.8 volt. As soon as the scale reaches 0.2 the film shutter is closed, the motor turned off, the scale returned to zero, the bridge voltage turned off, and the mercury bulb returned to the lower level.

In order to verify the uranium curve a small amount of the sample is removed and a known uranium solution added. The next polarogram should then show an increase in the previous uranium curve and a decrease in any other curve shown. It is necessary to repeat all the operational steps enumerated, after the film cartridge has been turned to the next position.

FILM DEVELOPMENT AND CURVE CALIBRATION.

After the desired number of polarograms have been taken the camera cylinder can be removed from the polarograph. The inner cylinder must not be removed from the outer cylinder except in a photographic darkroom. A Wratten Safelight Series OA is satisfactory for the E-1 bromide paper which is supplied for the polarograph. The film is developed in a tray containing D-72 developer diluted 1 : 1 until a good outline of the trace is observable and then placed in the F-5 fixing solution for 15 to 20 minutes. It is next washed thoroughly and dried.

Many methods for calibrating the current step are recommended. The method used in this work is shown in Figure 1.

(1) Draw straight line extensions (a) and (b) on the principle slopes which are formed before and after the current step. (2) Draw straight line extension (c) along the current step slope. (3) Draw horizontal line (d) through the point (p). (4) Drop a perpendicular line (e) from the point (p_1) to the horizontal line (d). The length of the line (p_1,p_2) gives the height of the current step in millimeters.

STANDARDIZATION OF CURVES

Solutions of various concentrations were prepared from a stock solution. The concentration of the stock solution was determined by the standard gravimetric procedure which was carried out in the following steps.

By calculation it was determined that 17.8178 grams of $(CH_3COO)_2UO_2 \cdot 2H_2O$ in 250 ml of solution would give a concentration of 40 grams of uranium per liter. To standardize the stock solution, 25 ml of the solution were transferred by means of a Normax pipette to a 250 ml Exax volumetric flask and the solution adjusted to 250 ml at 20°C. Two 50 ml aliquots were taken by means of a 50 ml Normax pipette. Both aliquots were evaporated almost to dryness and 15 ml of conc HNO_3 added. The solution was then boiled to destroy the acetate.

The two aliquots were heated to near boiling and the uranium was precipitated as $(NH_4)_2U_2O_7$ by using 6N NH_4OH. The precipitate was collected on No. 42 Whatman paper. The crucibles were ignited over Meker burners, cooled, and weighed. The precipitates were ignited 45 minutes at full blast to form U_3O_8, cooled, and weighed.

	Sample 1	Sample 2
wt of crucible and sample	17.3592 g	17.1840 g
wt of crucible	17.1250 g	16.9498 g
wt of sample	.2342 g	.2342 g

Uranium in sample: .2342 g x 8480 x 5 x 40 = 39.72 g/liter.

From this standardized stock solution one liter of solution containing 400 micrograms of uranium was prepared. The calculated amount of original stock solution was first fumed to dryness with conc H_2SO_4. To make a supporting electrolyte of 5% H_2SO_4, 50 ml of conc H_2SO_4 are required per liter of solution. The UO_2SO_4 was dissolved in the 50 ml of conc acid and the solution diluted to 1 liter at 20°C.

Various samples were prepared from the 400 microgram stock solution ranging from 100 micrograms to 400 micrograms. Here, too, special attention was paid to temperature and all work was done with Normax pipettes and Exax flasks. A portion of the 400 microgram solution was transferred to a dry 500 ml ground glass stoppered Erlenmeyer flask and immersed in ice water until the temperature of the solution reached 17–19°C.

An amount approximately required for the solution to be prepared was transferred to a small beaker and the necessary amount pipetted by the proper combination of 50, 25, 10, and 5 ml pipettes, which had previously been rinsed with some 400 microgram solution. Finally, the volume was adjusted to 100 ml by diluting with 5% H_2SO_4 also cooled to near 20°C and the polarogram made. The solutions were not taken in order from 100 micrograms to 400 micrograms but were chosen at random. The calibrated polarograms are shown in Figure 2 and the tabulation of results is given in Table 1.

Table 1.

Concentration of solution (γ/ml)	Height of curve (mm)	Corrected concentration	Deviation
100	18.0	96.7	+3.3
120	23.0	123.5	-3.5
140	25.4	136.4	+3.6
160	29.8	160.0	0.0
180	34.6	185.8	-5.8
200	37.2	199.8	+0.2
220	41.2	221.2	-1.2
240	44.0	236.3	+3.7
260	50.8	272.8	-12.8
280	53.0	284.6	-4.6
300	50.4	270.6	+29.4
320	59.4	319.0	+1.0
340	59.4	319.0	+21.0
360	70.6	379.0	-19.0
380	74.0	397.4	-17.4
400	74.2	398.5	+1.5
4000	745.0		

$4000 \div 745.0 = 5.37\ \gamma/\text{mm}$ mean absolute deviation = $\pm 8.68\gamma$

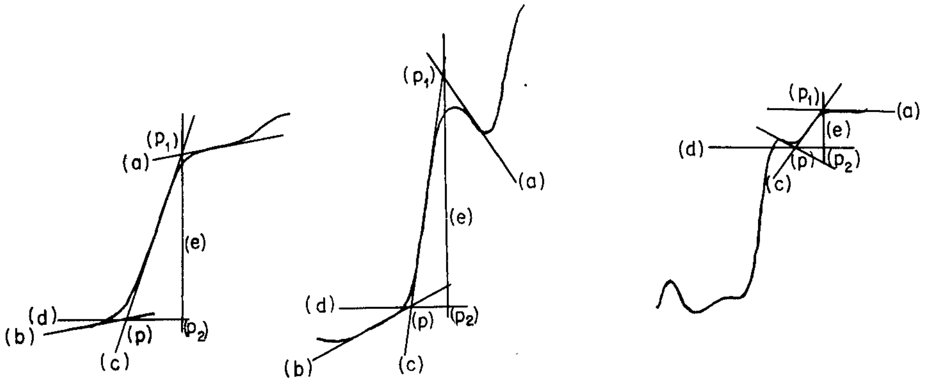

Figure 1.

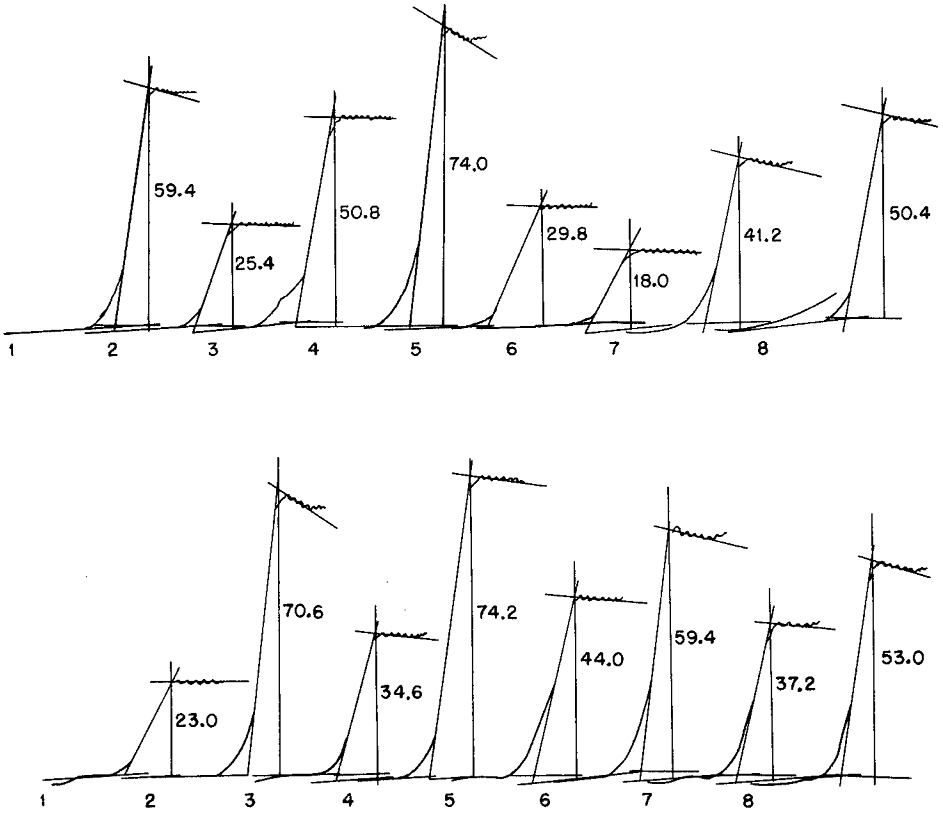

Figure 2.

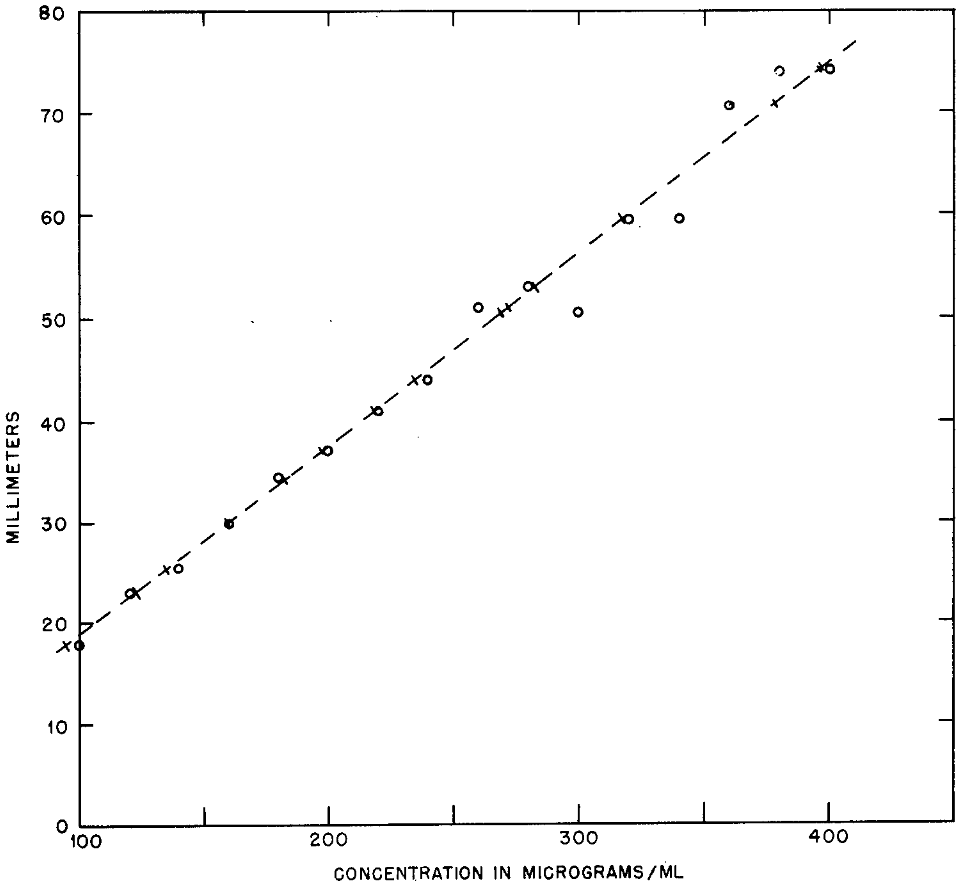

Figure 3.

From this data it was found that 1 mm on the curve represented 5.37 micrograms of uranium. A mean absolute deviation of ± 8.6 micrograms existed over the range of concentrations investigated. Therefore, an average error of about 3% can be expected. For this work a current sensitivity of 20 was used. The mercury head was 48.5 cm and the dropping rate was 3.4 sec at 0.0 volt. Restandardization must be done whenever the height of the mercury head or the capillary is changed. The results of the standardization is shown graphically in Figure 3.