

Table I. Determination of Diffusion Coefficients

Electrode Diameter, Inch	Concn. <i>o</i> -DIA ^a	Technique	$D \times 10^5$, Sq. Cm./Second
$\frac{3}{16}$	$4.0 \times 10^{-4}M$	RDE, 9 RPS	0.370
$\frac{1}{8}$	$4.0 \times 10^{-4}M$	RDE, 9 RPS	0.366
$\frac{3}{16}$	$4.0 \times 10^{-4}M$	RDE, 3 RPS	0.363
$\frac{1}{8}$	$2.3 \times 10^{-4}M$	RDE, 27 RPS	0.364
$\frac{1}{4}$	$4.0 \times 10^{-4}M$	Linear diffusion ^b	0.367
$\frac{1}{4}$	$1.0 \times 10^{-3}M$	Linear potential sweep ^c	0.373
$\frac{1}{4}$	$1.0 \times 10^{-3}M$	Linear diffusion	0.381
$\frac{1}{4}$	$1.0 \times 10^{-4}M$	Linear potential sweep	0.361

^a Oxidation of *o*-dianisidine in 1*M* sulfuric acid.^b Shielded electrode, evaluated from (*it*^{1/2}) curve.^c Shielded electrode, evaluated from peak polarogram.

All measurements made at 25° ± 0.5° C.

normally escapes detection. By applying E_1 to the inner disk and E_2 to the outer ring and increasing the rotation velocity, it is possible to sweep C to the outer ring where it can be unequivocally detected (4).

The simplicity of carbon paste rotated disk electrodes seems to offer distinct advantages in electrochemical studies. A detailed report of the operation of such electrodes will soon be given.

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LITERATURE CITED

- (1) Adams, R. N., *ANAL. CHEM.* **30**, 1576 (1958).
- (2) Bircumshaw, B. L., Riddiford, A. C., *Quart. Rev.* **6**, 157 (1952).

- (3) Frumkin, A., Nekrasov, L., Levich, V. G., Ivanov, Ju, *J. Electroanal. Chem.* **1**, 84 (1959).
- (4) Galus, Z., Adams, R. N., Abstracts, 140th Meeting, ACS, Chicago, Ill., September 1961.
- (5) Galus, Z., Alden, J. R., Adams, R. N., unpublished data, Univ. of Kansas.
- (6) Gregory, D. P., Riddiford, A. C., *J. Chem. Soc.* **1956**, 3756.
- (7) Jordan, J., Javick, R. A., Ranz, W. E., *J. Am. Chem. Soc.* **80**, 3846 (1958).
- (8) Kholpanov, L. P., *Zhur. Fiz. Khim.* **35**, 1538 (1961).
- (9) Koutecky, J., Levich, V. G., *Ibid.*, **32**, 1565 (1958).
- (10) Levich, V. G., *Acta Physicochim. U.R.S.S.* **17**, 257 (1942).
- (11) Levich, V. G., "Fiziko-khimicheskaya gidrodinamika (Physico-Chemical Hydrodynamics)," p. 77, Godudarstvennoe, Izdatel'stvo Fizikomatematicheskoi Literatury, Moscow, 1959.
- (12) Newson, J. D., Riddiford, A. C., *J. Electrochem. Soc.* **108**, 695 (1961).
- (13) Olson, C., Adams, R. N., *Anal. Chim. Acta* **22**, 582 (1960).

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Pyrolytic Separation of Ruthenium

SIR: Several methods have been presented (1,2,3) for the preparation of ruthenium from simple salts by wet oxidation and volatilization processes, but little has been reported on the adaptation of these methods to the separation of ruthenium from various nitroso complexes. The isolation of ruthenium in a spectrophotometrically measurable form from the nitroso-sulfate or nitroso-chloride complexes is difficult. When perchloric-sulfuric acid oxidation was applied to samples of ruthenium-nitroso complexes in uranyl sulfate solutions, recovery of ruthenium was low (less than 20%).

Fusion pyrolysis at 1000° C., utilizing a sodium bismuthate flux coupled with a sweep of moist oxygen, converted microgram quantities of ruthenium as the complex nitroso compounds to the volatile tetroxide, RuO₄. A fused silica boat must be used to contain the sample and flux; otherwise, a creeping of the flux occurs. A separate boat is used

for each analysis because of cracking during the cooling cycle to room temperature. The general apparatus has been described previously (5).

The stream of moist oxygen carries the volatilized RuO₄, formed in the flux, to a trap of 3*N* HCl saturated with SO₂ where it is removed from the gas stream.

PROCEDURE

Ruthenium Nitroso Salts. Transfer a test portion of the sample, estimated to contain from 50 to 400 µg. of ruthenium, to a fused silica boat. Add one drop of concentrated H₂SO₄, one drop of phenolphthalein, and then add 50% NH₄OH dropwise until the solution is alkaline. Evaporate the solution to dryness under an infrared heat lamp. Break up the residue remaining in the boat after the evaporation; then add 8 grams of NaBiO₃ flux to the boat and mix the flux and the residue thoroughly.

Assemble the pyrolysis apparatus as previously described (5). Place the

silica boat containing the sample in the combustion tube and carry out the pyrolysis at 1000° C. for 75 minutes with moist oxygen flowing through the apparatus at a rate of approximately 1 to 2 bubbles per second. Pass the off-gas into 20 ml. of 3*M* HCl (SO₂ saturated) which is contained in a 25-ml. graduated cylinder. Throughout the pyrolysis, keep SO₂ bubbling through the HCl solution at a flow rate of 1 to 2 bubbles per second. At the end of the pyrolysis period, turn off the furnace and stop the flow of oxygen through the apparatus. Also, terminate the flow of SO₂ through the solution of HCl. Rinse the quartz delivery tube with 15 ml. of the HCl-SO₂ solution in a 50-ml. volumetric flask. To accomplish this, apply suction with a rubber bulb to the opposite end of the quartz tube and then draw the wash solution into the delivery tube several times. Withdraw the delivery tube and add the solution from the graduated cylinder to the wash solution in the 50-ml. volumetric flask. Proceed with the spectrophotometric determination as described elsewhere (4).

Application to Samples. Tests were made of the applicability of the method to the determination of ruthenium as the nitroso-sulfate complex. Standard samples of uranyl sulfate were prepared which contained approximately 100 mg. of uranium, 100 μ g. each of iron, nickel, and chromium, and known quantities of ruthenium nitroso sulfate. The ruthenium nitroso sulfate was prepared by the procedure of Griess (4). The samples were pyrolyzed according to the recommended procedure, and the ruthenium was determined colorimetrically with 2-nitroso-1-naphthol. Results are shown in Table I. Over the range of about 20 to 200 μ g. of ruthenium, an average recovery of 95% was realized with a relative standard deviation of approximately 13%.

Although the method was applied only to the determination of ruthenium in solutions of uranyl sulfate, it appears that it would be used for the analysis of other types of samples which were not tested. Substances expected to in-

Table I. Determination of Ruthenium in Synthetic Samples Containing Ruthenium Nitroso Sulfate after Pyrolytic Separation

(Samples contain 100 mg. of uranium)

Ruthenium		
Added, μ g.	Found, μ g.	Recovery, %
20 ^a	20	100
29	37	120
68	70	103
100 ^a	103	103
	110	110
100	110	110
	83	83
	85	85
114	113	99
	96	84
228	198	87
Average		95
Standard deviation		13

^a Ru added as RuCl₃.

terfere include, in particular, other platinum metals of the platinum group

which would be volatilized along with the ruthenium.

LITERATURE CITED

- (1) Banks, C. V., O'Laughlin, J. W., *ANAL. CHEM.* **29**, 1412 (1957).
- (2) Hoffman, J. G., Lundell, G. E. F., *J. Research Natl. Bur. Standards* **22**, 465 (1939).
- (3) Larsen, R. P., Ross, L. W., Kesser, G., *ANL* **5810** (1957).
- (4) Manning, D. L., Menis, O., *ANAL. CHEM.*, **34**, 94 (1962).
- (5) Powell, R. H., Menis, O., *Ibid.*, **30**, 1546 (1959).

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A Simple Method of Temperature Programming for Gas Chromatography

SIR: In my recent article [*ANAL. CHEM.* **33**, 1632 (1961)] the instrument used was a Perkin-Elmer Model 154D Vapor Fractometer. It was stated that the precaution of shutting off the detector while the gas flow was interrupted was not observed, but no difficulties were encountered because of this. Since the standard instrument, as received by our laboratory, was equipped with thermistor beads, no specific

mention was made of the fact. However, as called to my attention by a reader, if an instrument equipped with hot wire filaments employs this technique, the detector should be shut off while the gas flow is interrupted, or the filaments will be damaged.

The article was describing a means of temperature programming which required absolutely no modification of the basic instrument. The only prereq-

uisite is that the instrument be equipped with a gas sampling valve similar to that found on Perkin-Elmer Vapor Fractometers or some other suitable means of stopping the flow of carrier gas.

The caption for Figure 1 should read "with (right) and without (left)."

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Polarography of Solutions Containing Elemental Sulfur and Metal Ions

SIR: Several workers have shown that the reaction of metal ions with reduction products at a dropping mercury electrode results in nonadditivity of polarographic diffusion currents. For example, precipitation of cadmium ions from solution with hydroxide ion from the reduction of iodate causes the increase in current at the iodate potential to be smaller than expected (1). Similarly, the diffusion current at the selenite

reduction potential does not show the expected increase for solutions containing the ammoniacal cupric ion because of the precipitation of cupric selenide (2). Also, for solutions containing tellurite and plumbite ions, nonadditivity of diffusion currents results from precipitation of lead telluride upon tellurite reduction (2). Diffusion currents so affected by secondary reactions have been termed "latent limiting cur-

rents" by Kemula and Grabowski (3).

Similar effects have recently been observed in our laboratories in polarography of solutions containing elemental sulfur and metal ions. When the metal ion is reduced at the more negative potential, the sulfur wave is much smaller than usual. If sulfur is reduced first, the increase in current for the metal reduction is less than expected. This behavior is believed to be due to