observed densities and the calculated density obtained by inserting the observed limiting values of $\Delta d/f_2$ and the appropriate values of V_1, V_2 and d_1 in equation 3 below.

$$\frac{\Delta d}{f_2}(\text{lim.}) = \left(\frac{V_2}{V_1}\right)(d_2 - d_1) \qquad (3)$$

TABLE II

Substance	d_2 (obsd.)	d_2 (lim.)	$\frac{\Delta d}{f_2}$ (lim.)	$\frac{\Delta d^*}{f_2}$	$\sum\frac{\Delta d}{f_2}$(lim)
Chlorobenzene	1.10	1.10	0.260	0.260	...
Dichlorobenzene	..	1.27	.519	(.519)	0.520
Benzotrifluoride	1.17	1.15	.398	.423	...
o-Chlorobenzotrifluoride	1.36	1.32	.686	.720	.658
m-Chlorobenzotrifluoride	1.33	1.29	.657	.695	.658
p-Chlorobenzotrifluoride	1.33	1.29	.658	.695	.658
Benzotrichloride	1.36	1.38	.802	.803	...
o-Chlorobenzotrichloride	1.51	1.52	1.10	1.08	1.06
m-Chlorobenzotrichloride	1.48	1.48	1.06	1.05	1.06
p-Chlorobenzotrichloride	1.47	1.48	1.06	1.05	1.06
Benzotribromide	..	2.22	2.23	(2.23)	..
o-Chlorobenzotribromide	2.26	2.34	2.54	2.48	2.49
m-Chlorobenzotribromide	2.21	2.28	2.50	2.45	2.49
p-Chlorobenzotribromide	..	1.27	2.50	(2.50)	2.49

The last column in Table II, $\Sigma\Delta d/f_2$(lim.), is obtained by adding the observed values of $\Delta d/f_2$(lim.) for the parent molecules: *viz.*, for *o*, *m*- and *p*-chlorobenzotrichloride the value of $\Delta d/f_2$(lim.) for chlorobenzene and benzotrichloride. The additivity of these values is quite good for the *meta* and *para* derivatives, and for the *ortho* cases is somewhat less satisfactory. In data for another series of measurements made on benzene solutions of the *o*-, *m*-, *p*-, fluoro-, chloro- and bromobenzotrifluorides in which the densities of the solutions were not so precisely determined as in the present work it was found that, including the *ortho* cases, the average deviation from additivity was approximately ±2.5%. In view of this it appears that the observed additivity of the limiting value of $\Delta d/f_2$ for a given solvent may be a rather general phenomena and thus may be useful in predicting densities of dilute solutions of derivatives if the appropriate values for the parent substances are known. A comparison of the observed and calculated values of the densities in Table II indicates that, in the series examined, approximate values of the density of the pure substances can be calculated by the method employed.

Examination of the graphs in Fig. 1 indicates that a reasonably good limiting value of $\Delta d/f_2$ can be obtained from a single measurement of a dilute solution if this is corrected assuming the slope of the $\Delta d/f_2$ *vs.* f_2 line is the same as for $\Delta d^*/f_2$ *vs.* f_2. If the value of $f_2((V_2/V_1) - 1)$ is small enough so that $1/[1 + f_2((V_2/V_1) - 1)]$ can be replaced by $1 - f_2((V_2/V_1) - 1)$ this slope is given by $(V_2/V_1)^2(d_2 - d_1)(V_2 - V_1)$.

The work of Kopp, LeBas and Traube on the additivity of atomic and molecular volumes has been reviewed by Smiles[4] and Kremann[5]; however, there appears to be no simple evident relation between the molar volume additivity and the additivity of $\Delta d/f_2$(lim.).

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, NORTH CAROLINA

---

(4) S. Smiles, "Relations Between Chemical Constitution and Some Physical Properties," Longmans, Green and Company, New York, N. Y., 1910, Chap. IV.

(5) R. Kremann, "Physikalischen Eigenschaften und Chemischer Konstitution," Theodor Steinkopff, Leipzig, Germany, 1937, Chap. III.

Radiochemical Purification of Nickel in Macro Quantities

BY S. E. SINGER[1] AND M. H. KURBATOV

RECEIVED APRIL 15, 1954

The authors were faced with the problem of purifying approximately 39 grams of neutron irradiated nickel to be used for the study of radiative electron capture in nickel-59.[2] Observation of the disintegration of this species is made difficult by the fact that the long half-life of 7×10^4 years together with the relatively low thermal neutron cross-section of 4.2 barns for nickel-58 restricts the amounts of activity obtainable to very small quantities. In addition, the phenomenon of radiative electron capture can be shown to amount to only 8×10^{-4} of the ordinary electron capture activity of nickel-59.[3] Thus in spite of the fact that the nickel sample was large and had been irradiated for 28 days with the highest thermal neutron flux then available (7×10^{12} neutrons/cm.^{2}/sec.), the total radiative electron capture activity was calculated to be only 1.2×10^{-7} curie. It was therefore necessary to undertake purification of the entire 39-g. sample in order to provide sufficient activity for study.

The classical procedure for the separation of nickel as the dimethylglyoxime complex is ordinarily restricted to amounts of nickel of the order of 10 to 30 mg. because of the low solubility of the reagent and the voluminous precipitate formed. Bickerdike and Willard[4] have shown that precipitation of this complex from homogeneous solution permits analysis of 100-mg. quantities of nickel. Similar results were obtained by Sweet and Harris.[5]

Experimental

A preliminary exploration of the possibilities of such a method for larger quantities of nickel was carried out as follows: A nitric acid solution containing approximately 4 g. of common nickel was diluted to one liter and the *p*H of the solution lowered to 0.8 with hydrochloric acid. The solution was placed in a five-liter round-bottom flask, 1200 ml. of a saturated solution of dimethylglyoxime in 95% ethanol were then added, followed by 200 g. of urea slurried in 200 ml. of water. The mixture was refluxed at the boiling point until samples of the supernate gave no test for nickel upon the addition of ammonium hydroxide. At *p*H 3.2, the supernate gave a positive test. The next check, at *p*H 5.9, gave a negative test for nickel. The latter *p*H was reached after approximately three hours of boiling. The resulting nickel complex was filtered through a medium porosity sintered glass funnel and washed with 50% ethanol to remove excess dimethylglyoxime. The precipitate consisted of minute, needle-like, brownish-red crystals, and was far less bulky than the usual nickel–dimethylglyoxime complex.

---

(1) Headquarters, Air Force Special Weapons Center (ARDC), Kirtland Air Force Base, Albuquerque, New Mexico.

(2) W. S. Emmerich, S. E. Singer and J. D. Kurbatov, *Phys. Rev.*, **94**, 113 (1954).

(3) J. M. Jauch, Oak Ridge National Laboratory Report 1102 (1951).

(4) E. L. Bickerdike and H. H. Willard, *Anal. Chem.*, **24**, 1026 (1952).

(5) W. F. Harris and T. R. Sweet, unpublished data.

The common nickel used in this experiment was prepared from nickel sheet metal. A spectrographic analysis of this material gave the following approximate composition: nickel > 99%; cobalt < 1%; iron < 1%; manganese < 0.1%; copper < 0.1%; chromium, Trace. A spectrographic analysis of the nickel–dimethylglyoxime complex obtained indicated no impurities except a trace of iron, estimated at less than 10^{-6} gram atom.

Further study of the purification of macro-quantities of nickel by this general method elicited the following facts, all of which are based on a three-liter reaction mixture 50% in alcohol which was refluxed in a five-liter round-bottom flask.

Solvent.—Isopropyl alcohol appeared to be preferable to ethanol as a solvent for the dimethylglyoxime reagent. The higher boiling point of isopropyl alcohol permits more rapid decomposition of urea. Further, while severe "bumping" was encountered when ethanol solutions were used, this problem did not arise to any appreciable degree with isopropyl alcohol.

Purification with Dimethylglyoxime Solutions.—The maximum amount of nickel which can be precipitated by the use of equal volumes of nickel solution and an alcoholic solution of dimethylglyoxime is a function of the solubility of the dimethylglyoxime and the capacity of the reaction vessel. For a five-liter flask, this is of the order of 10 g. of nickel. Under these conditions, the precipitation of nickel is complete at a *p*H of 4.4.

Purification with Solid Dimethylglyoxime.—The reagent may be added as the solid slurried in alcohol. In this case the maximum amount of nickel which can be treated in a vessel of given size is primarily a function of the volume of the nickel complex. For three liters of 50% isopropyl alcohol in a five-liter flask the maximum permissible amount of nickel is more than 40 g. If solid dimethylglyoxime is used in an amount sufficient to keep the reaction mixture always saturated with this reagent, the reaction is complete at about *p*H 2.4. Under these conditions the nickel complex is usually contaminated with a small amount of dimethylglyoxime even after extensive washing with 50% alcohol (ethyl or isopropyl). The dimethylglyoxime can be removed readily by drying the precipitate at 130 to 150°.

Initial *p*H.—If the *p*H of the reaction mixture is sufficiently low at the start of the reaction, true precipitation from homogeneous solution is obtained, that is to say, there is no precipitation of the nickel complex whatever until an appreciable decomposition of the urea has been effected. Using dimethylglyoxime in isopropyl alcohol solution, this *p*H is approximately 2. For solid dimethylglyoxime, this *p*H is about 0.8. Under these conditions the precipitate is highly crystalline, dark and compact. If the initial *p*H of the reaction mixture is slightly higher, some precipitation occurs as soon as the dimethylglyoxime reagent is added. This can be termed "pseudo" precipitation from homogeneous solution. In this case the precipitate is slightly less crystalline, somewhat lighter in color, and slightly more voluminous.

Reflux Time.—The period of time that the reaction mixture must be refluxed to obtain complete precipitation of the nickel is a function of the initial *p*H, the amount of urea used, and the quantity of nickel to be complexed. In a typical separation using approximately ten grams of nickel, an initial *p*H of 2.0, 300 g. of urea, and a total volume of three liters, a *p*H of 6.2 was reached after refluxing for approximately five hours.

Purification of Active Nickel.—The principal radioactive contaminants present in the active nickel sample were known to be Co-58 and Co-60, in millicurie amounts, and microcurie quantities of Mn-54 and Fe-55. In addition, small amounts of Cr-51 and Fe-59 were present. Stable iron also was present in weighable quantities.

The active nickel was dissolved in dilute nitric acid, and iron was removed at low *p*H as the hydrous ferric oxide.

The nickel solution was diluted to approximately 1200 ml. and 100 mg. each of Co(II), Mn(II) and Cr(III) carriers were added. The *p*H was then reduced to 0.4 by the addition of concentrated hydrochloric acid, and the solution was transferred to a five-liter round-bottom flask. A slurry of 226 g. of dimethylglyoxime in 1500 ml. of isopropyl alcohol was then added, followed by 500 g. of urea slurried in 300 ml. of water. The mixture was refluxed at the boiling point until samples of the supernate did not give a test for nickel upon the addition of ammonium hydroxide. The mixture was cooled, filtered with suction through a medium porosity sintered glass funnel, and washed with 1500 ml. of 50% isopropyl alcohol. The washed precipitate occupied a volume of approximately 300 ml. It was dissolved in concentrated nitric acid, the resulting solution was diluted with water, filtered to remove dimethylglyoxime and oxidation and nitration products thereof, fresh carriers added, and the nickel reprecipitated with dimethylglyoxime as indicated above. This procedure was carried out a total of six times. The final precipitate was dried at 140° to remove excess dimethylglyoxime, and was then converted to nickel oxide.

The only active γ-emitting impurity detectable in the final sample was less than four counts per minute (1.5×10^{-9} curie) of Co-60 as measured with a γ-scintillation spectrometer capable of detecting as little as 4.8×10^{-10} curie of this species and comparable amounts of other γ-activities. This represents over-all purification against Co-60 by a factor of approximately 10^7.

The necessity for the large number of reprecipitations of the nickel complex carried out is attributed more to an inability to wash the large quantities of complex efficiently than to any serious retention of active species by the complex itself.

The fact that the dimethylglyoxime separation method described above was used successfully for the purification of an unusually large quantity of active nickel would appear to recommend this general scheme for use with the much smaller quantities more commonly encountered in radiochemical separations. The use of solid dimethylglyoxime would appear to be especially advantageous since thereby one can obtain complete precipitation of the nickel complex at a *p*H so low that carrying of other active cations can, in general, be expected to be minimized.

The authors are indebted to Mr. Bruce Murray for spectrographic analyses of nickel samples, and to Mr. W. F. Harris and Dr. T. R. Sweet for making available their unpublished data on the precipitation of nickel from homogeneous solution.

It is a pleasure to express our appreciation to the Ohio State University Development Fund for grants for research instruments.

DEPARTMENT OF CHEMISTRY
OHIO STATE UNIVERSITY
COLUMBUS, OHIO

The Single Sucrose Gradient as a Convection Barrier During Descending Boundary Preparative Electrophoresis[1]

BY SAM SOROF AND MARILYN G. OTT

RECEIVED MAY 12, 1954

Boundary electrophoresis as a productive preparative method has been hampered by the occurrence of convection, often long before maximum purity and yield have been attained. When the faster boundaries migrate into the bottom section of the electrophoresis cell, convection due to gravitational instability causes mixing of the descending and ascending solutions. Indistinguishable boundaries then make the isolation of highly purified fractions impossible. The onset of this convection may be postponed by compensating the descending

---

[1] Supported by grant 228A from the Damon Runyon Memorial Fund for Cancer Research, and an institutional grant from the American Cancer Society.