**Table VII. Relation of Ion Current to Disintegration Rate**

| Gas | Coulombs/Disintegration $\times 10^{17}$ | Curies/Ampere $\times 10^{-6}$ |
|---|---|---|
| Hydrogen | 2.12 | 1.275 |
| Methane | 3.09 | 0.874 |
| Propane | 3.49 | 0.775 |

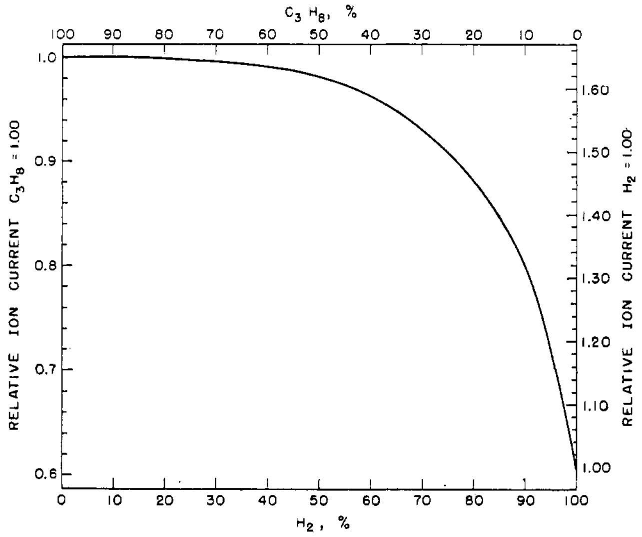

**Figure 2. Ion Currents at Saturation Voltage in Hydrogen-Propane Mixtures at 1 Atmosphere**

and from the relative ion currents given in Table II, the factors in Table VII have been computed.

The method of tritium assay which has been described is useful over at least a $10^8$-fold range of tritium activities. The lower limit is determined by the magnitude and reproducibility of the background current. In the authors' experience this can be easily maintained near $5 \times 10^{-16}$ ampere, of which $2 \times 10^{-16}$ ampere is caused by penetrating radiation, including cosmic rays, and $3 \times 10^{-16}$ ampere arises from soft radiation. If it is assumed that each ionizing event produces 300 ion pairs, a value between the 450 ion pairs produced (*21*) by a cosmic event and the 200 produced by a tritium disintegration, it can be calculated (*13*) that 13 tritium disintegrations per second ($4 \times 10^{-16}$ ampere in methane) can be determined with an accuracy of 1% for a time of measurement of 1 hour each for sample and background. The results in Table VI show that samples containing 25 disintegrations per second can be analyzed with this precision.

The maximum quantity of tritium which can be measured is that above which recombination cannot be prevented without using a collecting voltage so large as to cause leakage of current or multiplication of ionization. The data in Table III indicate that in hydrogen or methane saturation currents are obtained at moderate voltages for quantities of tritium up to 10 mc.

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# Cupferron and Neocupferron Complexes of the Rare Earth Elements

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**Cupferron and neocupferron show definite promise as precipitating reagents for the rare earth ions. The exact conditions of precipitation and the properties of the resulting complexes have not been reported in literature. In this work it was found that precipitation seems to be quantitative, but the precipitates are somewhat contaminated by coprecipitation. Ignition of the cupferrates and the neocupferrates to corresponding oxides yields analytical results which compare favorably with the oxalate method. The precipitates are somewhat soluble below pH 2.0 and the optimum pH for precipitation seems to be around 3.5. Conductimetric and high-frequency titrations indicate formation of an intermediate 1 to 1 complex $M\text{Cup}^{++}$.**

ALTHOUGH cupferron (ammonium nitrosophenylhydroxylamine) and neocupferron (ammonium nitrosonaphthylhydroxylamine) have been used extensively as precipitants for various inorganic cations during the past 40 years (*3*, *6*), very little work has been done so far on their reactions with the rare earth elements. The existence of cerium(III), cerium(IV) (*1*), and neodymium (*2*) cupferrates, as well as that of neodymium neocupferrate (*2*), has been reported in the literature. It was determined that the complexes were relatively insoluble in water and in organic solvents, but beyond that their properties were not described. This investigation was undertaken in order to obtain a more detailed picture of the types of complexes formed and of some of their properties.

### Table I. Cupferron Complexes

| Rare Earth | Color | M.Pt., ° C. | Oxide Found,[a] % | | Oxide Calcd. for $MCup_3$, % |
|---|---|---|---|---|---|
| | | | A | B | |
| La | Pale yellow | 182–4 | 25.03 | 24.90 | 25.24 |
| Ce(III) | Orange | 170–1 | 25.00 | 25.01 | 25.41 |
| Pr | Pale green | 186–7 | 24.57 | 24.53 | 25.51 |
| Nd | Pale pink | 185–6 | 25.24 | 25.24 | 25.97 |
| Sm | Yellow | 185–7 | 25.64 | 25.64 | 26.77 |
| Gd | Cream | 187–8 | 26.97 | 27.01 | 27.61 |

[a] $R_2O_3$ except $CeO_2$ and $Pr_6O_{11}$.

## EXPERIMENTAL

**Reagents.** Cupferron was obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio, and the neocupferron from the Distillation Products Industries, Rochester, N. Y. Both compounds were used without further purification.

The rare earths were obtained as oxides from the Fairmont Chemical Co., Newark, N. J., and were guaranteed to be 99% pure. The degree of purity was verified by converting the oxides to the chlorides by the usual method and determining the absorption spectra of the chloride solutions. The data thus obtained were compared with the values given by Moeller for the molar absorbancy indices of the rare earth ions in solutions (*4*). It was determined that less than 1% of other rare earth contaminants were present in each sample.

All other chemicals used were of analytical reagent grade.

**Absorption Spectra.** Absorption spectra were obtained on a Cary recording spectrophotometer Model 11. Calibrated silica cells of 1.00-cm. path length were used.

**Conductimetric and High-Frequency Titrations.** Conductometric studies were done on a Leeds and Northrup conductivity apparatus with precision of ±0.1%. The conductivity cells were calibrated with 0.01 and 0.001*N* potassium chloride and the temperature throughout the measurements was maintained at 25° ± 0.01° C. The high-frequency titration was carried out with a Sargent Model V oscillometer.

## PRECIPITATION AND ANALYSIS

**Experimental.** Approximately 1 gram of the rare earth oxide was dissolved in 50 ml. of 0.5*N* hydrochloric acid and a 0.2*M* solution of cupferron was slowly added until it was in excess. The resulting precipitate was filtered on a Büchner filter, repeatedly washed with water, and dried at 110° C. to constant weight. After weighing, the precipitate was ignited at 900° C. Usually 2 to 4 hours of heating were sufficient for a complete conversion to the corresponding oxide.

The neocupferron complexes were prepared in the same manner except for the preparation of the precipitating solution. Since neocupferron is only very slightly soluble in water, the solution was prepared by agitating approximately 10 grams of the reagent in 1 liter of water until saturation. The solution was filtered in order to remove the residue and was used immediately. The neocupferrates were dried in a desiccator at room temperature, since above 50° C. they started to decompose. Dry precipitates were ignited to oxides as described above.

**Results.** Table I summarizes some of the physical characteristics of the cupferron complexes.

It is seen from Table I that in all cases the amount of oxide obtained is somewhat lower than the theoretical amount. It is doubtful that this is due to absorbed moisture, as in some cases the precipitates were dried for as long as one month in a vacuum desiccator over barium oxide, and still analyzed low in oxide. The precipitates are probably contaminated by coprecipitating cupferron.

The properties of the neocupferron complexes are illustrated in Table II.

The melting points of the neocupferron complexes could not be determined. As the complexes were heated they gradually decomposed into a dark brown mass. It is seen that the coprecipitation is apparently less extensive in the case of the neocupferron than in the case of cupferron.

## EFFECT OF pH UPON PRECIPITATION

**Experimental.** A standard solution of samarium chloride was prepared by dissolving a known amount of samarium oxide in a slight excess of hydrochloric acid and diluting to 250 ml. Aliquots of 10 ml. were taken and diluted to 30 ml., and the rare earth ion was precipitated either with an excess of 0.2*M* cupferron solution or with a 10% oxalac acid solution. The resulting precipitates were converted to oxides by ignition at 900° C. to constant weight.

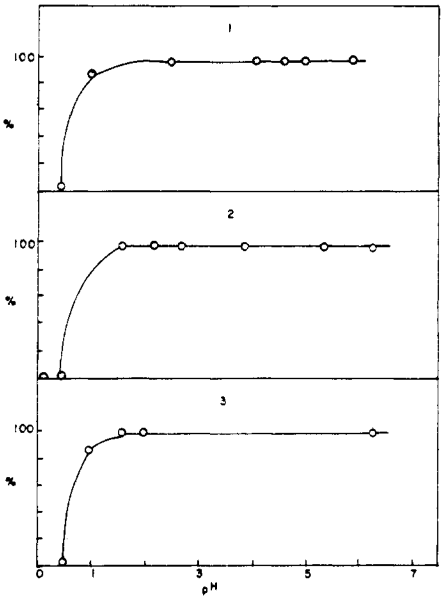

**Figure 1. Effect of pH on Precipitation of Rare Earths with Cupferron**

1. **Samarium chloride, 0.00981*M*; cupferron, 0.068*M***
2. **Neodymium nitrate, 0.0202*M*; cupferron, 0.077*M***
3. **Praseodymium chloride, 0.01946*M*; cupferron, 0.0903*M***

### Table II. Neocupferron Complexes

| Rare Earth | Color | Oxide Found[a], % | | Oxide Calcd. for $M(NeoCup)_3$, % |
|---|---|---|---|---|
| | | A | B | |
| La | Cream | 19.19 | 19.08 | 19.66 |
| Ce(III) | Tan | 19.69 | 19.75 | 19.80 |
| Pr | Yellow-green | 20.00 | 19.88 | 19.89 |
| Nd | Pale pink | 20.16 | 20.17 | 20.27 |
| Sm | Cream | 20.37 | 20.33 | 20.95 |
| Gd | Cream | 21.65 | 21.77 | 21.66 |

[a] $R_2O_3$ except $CeO_2$ and $Pr_6O_{11}$.

### Table III. Comparison of Cupferron and Oxalate Precipitations of Samarium

| Soln. 1[a] | | Soln. 2[b] | |
|---|---|---|---|
| Cupf. oxide obt., G. | Oxal. Oxide Obt., G. | Cupf. oxide obt., G. | Oxal. oxide obt., G. |
| 0.1037 | 0.1040 | 0.1004 | 0.1002 |
| 0.1038 | 0.1036 | 0.1003 | 0.1004 |
| 0.1035 | 0.1037 | 0.1001 | 0.1002 |
| 0.1038 | 0.1041 | 0.1003 | 0.1005 |

[a] 0.1038 Gram $Sm_2O_3$/10 ml.
[b] 0.1003 Gram $Sm_2O_3$/10 ml.

The effect of pH upon precipitation was studied for praseodymium, neodymium, and samarium salts. Buffer solutions in the pH range 1 to 6 were prepared according to standard directions (*9*). The procedure was to place 25 ml. of the rare earth solution, 50 ml. of the buffer solution, and 25 ml. of the cupferron solution in a 250-ml. beaker. The resulting precipitate was converted to the oxide in the usual manner. In all cases a three- to fourfold excess of cupferron was used.

**Results.** The comparison of the cupferron and oxalate precipitations is given in Table III.

It is seen from the results in Table III that the accuracy of the gravimetric determination with cupferron is certainly equal to that of the oxalate method.

The effect of pH is illustrated by Figure 1. Below pH 2 the precipitation is incomplete and the optimum pH for precipitation is around 3 to 4.

## SOLUBILITY STUDIES

**Experimental.** The solubilities of the rare earth cupferron complexes were determined by the indirect method of Pinkus and Martin (*5*). About 1 gram of the freshly precipitated, thoroughly washed rare earth cupferron complex was added to 500 ml. of conductivity water in a 1-liter flask. The flask was first heated for several hours at 40° C., then immersed in a constant temperature bath at 25 ± 0.02° C., and stirred for 48 hours. Preliminary studies showed that the equilibrium was established after this time interval. The suspension was allowed to settle for 12 hours and 150 ml. of the supernatant liquid were removed with a cotton-tipped pipet. The solution was evaporated to dryness, treated with 10 ml. of a 1 to 1 mixture of concentrated hydrochloric and nitric acids, and evaporated to dryness. After two such treatments, the residue was once more treated with 10 ml. of concentrated hydrochloric acid, again evaporated to dryness, and baked at 100° C. to ensure complete removal of hydrochloric acid. The residue of the rare earth chloride was dissolved in conductivity water and made up to 50 ml. The conductance of this solution was then measured and the solubility determined from the formula:

$$s = \frac{1000(L - L_w)}{3\lambda_0}$$

where $s$ is the solubility of the complex in moles per liter, $L_w$ is the specific conductance of water ($1.65 \times 10^{-6}$ mho), $L$ is the specific conductance of the solution, and $\lambda_0$ is the equivalent conductance at infinite dilution of the corresponding rare earth chlorides as recently determined by Spedding and coworkers (*7, 8*).

**Results.** The solubilities of the rare earth cupferrates are given in Table IV.

**Table IV. Solubilities of Rare Earth Cupferrates**

| Complex | Solubility, Moles/L. ($\times 10^5$) |
|---|---|
| $LaCup_3$ | 4.6 |
| $CeCup_3$ | 5.9 |
| $PrCup_3$ | 3.3 |
| $NdCup_3$ | 3.8 |
| $SmCup_3$ | 3.3 |

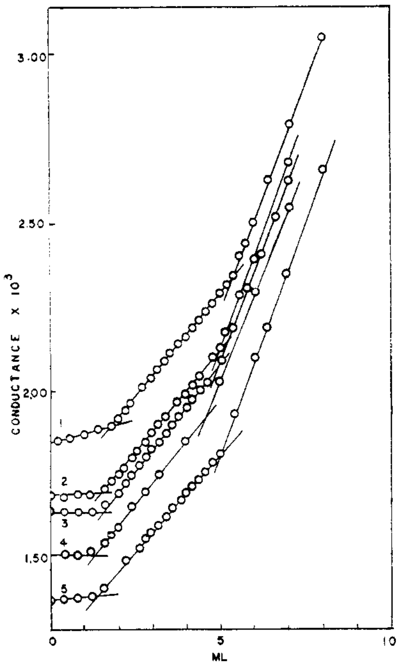

Figure 2. Conductometric Titration Curves of Rare Earths with Cupferron

1. $Nd(NO_3)_3$, 0.05099*M*; cupferron, 0.1473*M*
   1 to 1 complex, 1.75 ml. found; 1.73 ml. calculated
   1 to 3 complex, 5.30 ml. found; 5.19 ml. calculated
   (Ordinate shifted down by 2 × $10^{-4}$ mho)
2. $SmCl_3$, 0.04871*M*; cupferron, 0.1495*M*
   1 to 1 complex, 1.60 ml. found; 1.62 ml. calculated
   1 to 3 complex, 4.95 ml. found; 4.88 ml. calculated
3. $PrCl_3$, 0.04738*M*; cupferron, 0.1495*M*.
   1 to 1 complex, 1.60 ml. found; 1.58 ml. calculated
   1 to 3 complex, 4.85 ml. found; 4.75 ml. calculated
4. $CeCl_3$, 0.04673*M*; cupferron, 0.1592*M*
   1 to 1 complex, 1.40 ml. found; 1.47 ml. calculated
   1 to 3 complex, 4.45 ml. found; 4.40 ml. calculated
   (Ordinate shifted up by 5 × $10^{-4}$ mho)
5. $Gd(BrO_3)_3$, 0.04997*M*; cupferron, 0.1592*M*
   1 to 1 complex, 1.45 ml. found; 1.57 ml. calculated
   1 to 3 complex, 4.75 ml. found; 4.71 ml. calculated

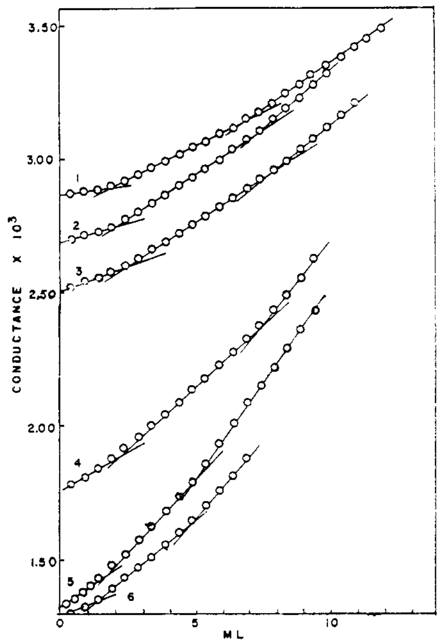

Figure 3. Conductometric Titration Curves of Rare Earths with Neocupferron

1. $SmCl_3$, 0.004642*M*; neocupferron, 0.01018*M*
   1 to 1 complex, 2.30 ml. found; 2.38 ml. calculated
   1 to 3 complex, 7.00 ml. found; 6.84 ml. calculated
2. $CeCl_3$, 0.004819*M*;. neocupferron, 0.01018*M*
   1 to 1 complex, 2.30 ml. found; 2.36 ml. calculated
   1 to 3 complex, 7.00 ml. found; 7.10 ml. calculated
3. $LaCl_3$, 0.005443*M*; neocupferron, 0.01018*M*
   1 to 1 complex, 2.60 ml. found; 2.67 ml. calculated
   1 to 3 complex, 8.00 ml. found; 8.02 ml. calculated
4. $PrCl_3$, 0.00478*M*; neocupferron, 0.01018*M*
   1 to 1 complex, 2.30 ml. found; 2.35 ml. calculated
   1 to 3 complex, 7.20 ml. found; 7.05 ml. calculated
5. $Gd(BrO_3)_3$, 0.003392*M*; neocupferron, 0.01018*M*
   1 to 1 complex, 1.65 ml. found; 1.66 ml. calculated
   1 to 3 complex, 5.00 ml. found; 5.00 ml. calculated
6. $Nd(NO_3)_3$, 0.003327*M*; neocupferron, 0.01018*M*
   1 to 1 complex, 1.60 ml. found; 1.63 ml. calculated
   1 to 3 complex, 4.90 ml. found; 4.90 ml. calculated

No great accuracy is claimed for these results; however, it is believed that they show at least the correct order of magnitude for the solubility.

It was found impossible to repeat these studies for the neocupferron complexes, as the solutions were unstable over a period of 2 days.

## CONDUCTOMETRIC STUDIES

**Experimental.** Conductometric and high-frequency titrations were carried out in order to determine whether any intermediate complexes are formed in solution between the rare earth ions and the cupferron or the neocupferron. In the conductometric titrations a stock solution of the rare earth salt was titrated with a cupferron or the neocupferron solutions of known concentration. The cupferron solutions were prepared by weight, while the neocupferron solutions were prepared as described previously and their concentration was determined by precipitation with an excess of a rare earth ion. The conductance values obtained were corrected for dilution. Because of the slight solubility of the neocupferron in water the solutions used were quite dilute.

**Results.** The results of the conductometric titrations and of a high-frequency titration are given in Figures 2, 3, and 4. Figure 2 shows that there is a definite break in the curve after one equivalent of cupferron is added. Up to that point no permanent precipitate is formed in solution, but when the reagent is added in excess of 1 to 1 ratio, a permanent precipitate begins to form and increases in size until three equivalents of the cupferron are

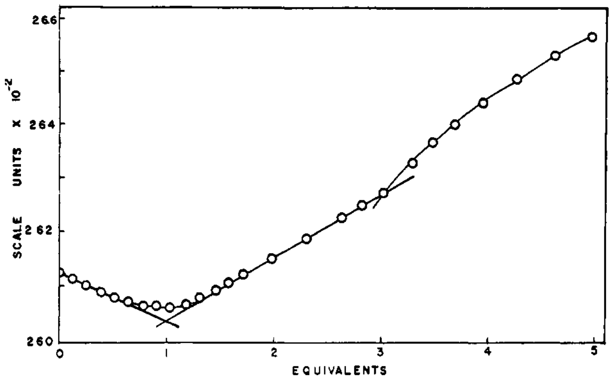

**Figure 4. High-Frequency Titration of Praseodymium Chloride with Cupferron**

1 to 1 complex: $PrCl_3$, 0.04738*M*; 1.50 ml. cupferron, 0.1573*M*
1 to 3 complex: $PrCl_3$, 0.04738*M*; 4.65 ml. cupferron, 0.1573*M*

added, when, presumably, the precipitation is complete. The neocupferron titration curve illustrates the same mode of behavior, although somewhat less clearly. High-frequency titration of praseodymium chloride verifies the intermediate formation of the 1 to 1 complexes, $MCup^{++}$ and $M(NeoCup)^{++}$.

## CONCLUSIONS

Cupferron and neocupferron seem to be excellent precipitating agents for the rare earth ions, provided that no interfering substances are present in the solution. Since cupferron and neocupferron are fairly general precipitating agents for many metal ions, it is obvious that they cannot compete with oxalic acid when the rare earth ions are to be separated from other impurities. However, in the absence of impurities and when only a small amount of rare earth is present in solution (2 to 50 mg.), the relatively large volume of precipitate and the ease with which it can be washed and filtered make the determination somewhat more accurate than the oxalate precipitation.

Apparently, under precipitation conditions describe here, considerable amount of coprecipitation makes it impossible to determine accurately the amount of the rare earth present from the weight of the dried precipitate. However, ignition to the oxide is rapid and yields very satisfactory results.

## ACKNOWLEDGMENT

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# Replacement of Lead Peroxide in Carbon, Hydrogen Microdetermination

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**When organic compounds containing 20 to 50% of nitrogen are analyzed by the micro carbon-hydrogen technique employing lead peroxide for absorption of nitrogen oxides, the carbon values tend to be high. This Pregl absorbent has been successfully replaced by trishydroxylamine phosphate contained in a tube interposed between the tubes used for absorption of water and carbon dioxide. Sulfamic acid also has been used, but its capacity for removal of nitrogen oxides is low, although its efficiency is high. The long absorptive life and the efficient removal of nitrogen oxides by the hydroxylamine salt commend its use when carbon values within a precision of 2% relative error are required for organic compounds which are high in nitrogen content. Moreover, elimination of the lead peroxide tends to increase the precision of the analytical results for nitrogen-free samples, since careful temperature equilibration of water and carbon dioxide versus the peroxide is no longer necessary.**

MANY attempts have been made to replace the troublesome lead peroxide by an alternative absorbent for nitrogen oxides in the microcombustion of organic compounds containing nitrogen. These variations in the carbon-hydrogen determination have been reviewed by Elving and McElroy (*7*), by Belcher and Ingram (*3*) and, most recently, by Backeberg and Israelstam (*2*). Opinions are divided between those who believe that nitrogen oxides should be removed in the absorption train, and those who recommend absorption or destruction of the nitrogen oxides within the combustion tube.

The use of metallic copper within the combustion tube for reduction of nitrogen oxides has recently been revived and adapted to the micro scale by Kainz (*13*). This worker claims that the copper (heated to 500° C.) is effective for 12 analyses, after which it is quickly and easily regenerated by passing hydrogen through the combustion tube. Previously, Millin (*17*) had used silver (at a lower temperature) for decomposition of the nitrogen oxides. However, Backeberg and Israelstam (*2*) believe that Millin's results were satisfactory, not because of the silver, but because that part of the copper oxide closest to the sample was reduced by the vapor of this distilling sample. The observation that silver alone is ineffective when nonvolatile samples are being analyzed has been confirmed here.

Despite opinions to the contrary (*2*), nitrogen oxides may be removed satisfactorily by absorbents outside the combustion tube (*16*). Such absorbents are interposed between the water and the carbon dioxide absorption tube. Elving and McElroy (*7*) recommend the use of sulfuric acid solutions of potassium dichromate or permanganate. Dombrovski (*6*) uses *p*-aminoazobenzene moistened with a saturated solution of boric acid and potassium dichromate, but this absorbent is exhausted after