

water and allow it to stand in contact with the excess chloride ions that have been carried over from the saturated solution, for 30 min. Finally, rinse the electrode with distilled water and place it in distilled water until it is used. The efficiency of the electrode is not impaired if the silver-chloride coating is not uniform. It is important, however, that care be taken to insure that it does not dry out. Electrodes that have been prepared in the above manner have been used for several weeks before they have been recoated.

Voltage measurements can be made, most conveniently, on the millivolt range of a pH meter.⁵ However, extreme accuracy requires that a slide wire potentiometer be used. To determine chloride concentration, connect the silver-silver chloride electrode to the positive binding post of the measuring instrument, the reference electrode to the negative binding post, and immerse the two electrodes in the unknown solution. The voltage developed across the electrodes is plotted on the concentration curve, and the unknown concentration is read directly. The electrodes should be rinsed with distilled water and blotted dry with a cleansing tissue between each two determinations. Table 1 shows the voltages developed by pure chloride solutions of various concentrations. Table 2 shows the voltages and the equivalent chloride concentrations for two different dilutions of the same blood serum. Several determinations of chloride in thoracic duct fluid and in buffered extracts of dry muscle tissue have been made. In every case, no drift was observed. The chloride concentration in thoracic duct fluid is identical with that of the corresponding blood serum, and the chloride of the muscle checks with values that have been found in the literature. Urine chloride has also been determined.

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⁵ The Beckman Model G was used.

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A Simple Method for the Calculation of Electrode Potentials in Polarography¹

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In polarographic work it is frequently necessary to convert applied voltage to electrode potential. This is accomplished by subtracting the product of current i , and total circuit resistance, R , from the applied voltage. This product is referred to as the iR factor. Its evaluation is a cumbersome operation and involves the separate experimental determinations of the current

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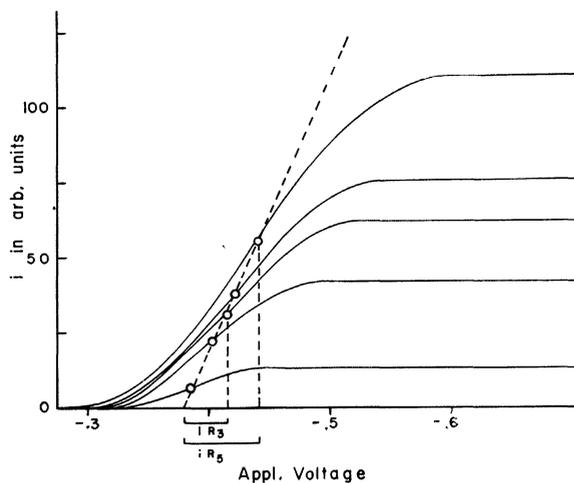


FIG. 1. Five concentrations of $\text{Pb}(\text{NO}_3)_2$ buffered to pH 6.8.

and of the resistance. The proposed method is simpler, because the iR factor can be obtained directly from a polarogram employing the low-voltage range customary in polarography;² thus the iR factor can be evaluated without the separate determination of either i or R .

The electrode potential corresponding to a given ratio of oxidant to reductant is a characteristic constant of a given substance and is independent of the concentration. An easily measured potential of this kind is the half-wave potential, where the ratio of oxidant to reductant is unity for all substances that are reducible or oxidizable at the electrode. If, however, current-voltage curves of the same substance are

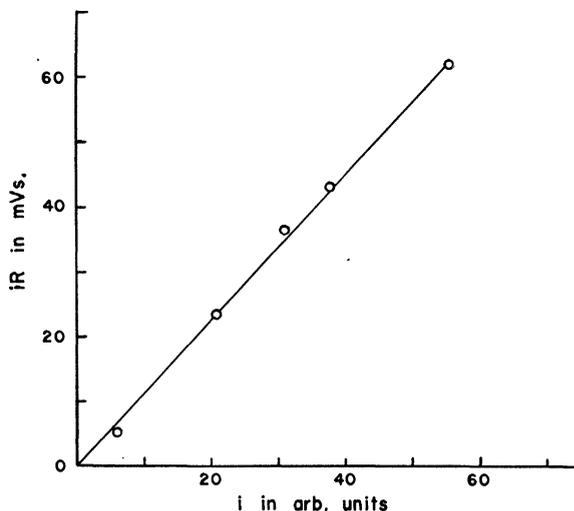


FIG. 2. Calibration curve constructed on the basis of Fig. 1.

² Müller's determination of the iR factor involves the application of higher voltages. O. H. Müller, *The Polarographic Method of Analysis*, p. 97. Easton, Pa.: Chemical Education Pub., 1951.

recorded at different concentrations, a gradual shift of the half-wave potential is observed with increasing concentration. This shift is entirely due to the increase of the iR factor, and for constant resistance the shift is a linear function of the current i . If the current values corresponding to the "half-wave voltages" are connected by a straight line, the intercept of this line with the voltage axis will be the true half-wave potential of the substance (Fig. 1); since at this point i is zero, iR must also be zero. The difference between the half-wave voltage and the thus determined half-wave potential for any particular curve will be the iR correction corresponding to the current value in question. It can readily be seen that if the resistance is kept constant, iR will depend solely on i .

Although the half-wave potential represents a convenient reference value to be used in constructing such a plot, it is emphasized that the same slope will be obtained if any other set of homologous points, that

is, current values corresponding to some constant ratio of oxidant to reductant, are connected. The intercept with the voltage axis in such a case will be the electrode potential for that particular ratio. It follows, therefore, that *any* measured i value is displaced along the voltage axis by an amount iR , which is determined entirely by i .

If the iR factors thus determined are plotted against i (Fig. 2), the voltage correction can be read from the graph for any i value. Since only voltage differences are calculated in the evaluation of iR , the factors determined by this method are independent of the nature of the substance employed for the determination of the half-wave shifts; and as long as the resistance and the galvanometer sensitivity are constant, the factors are applicable to all current values. If the current is expressed in amperes, the slope of the iR/i plot will give the resistance of the circuit in ohms.

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Communications

Rare-Earth Mineral Deposits of the Mountain Pass District, San Bernardino County, California

BASTNAESITE, a rare-earth fluorocarbonate, was found in the Mountain Pass district in April, 1949. Subsequent geologic mapping has shown that rare-earth mineral deposits occur in a belt about 6 mi long and $1\frac{1}{2}$ mi wide. One of the deposits, the Sulphide Queen carbonate body, is the greatest concentration of rare-earth minerals now known in the world.

The Mountain Pass district is in a block of pre-Cambrian metamorphic rocks, bounded on the east and south by the alluvium of Ivanpah Valley, and separated on the west from sedimentary and volcanic rocks of Paleozoic and Mesozoic age by the Clark Mountain normal fault; the northern boundary of the district is a conspicuous transverse fault. The pre-Cambrian metamorphic complex comprises a great variety of lithologic types.

The rare-earth-bearing carbonate rocks are spatially and genetically related to potash-rich igneous rocks of probable pre-Cambrian age that cut the metamorphic complex. The larger potash-rich intrusive masses, 300 ft or more wide, comprise one granite, two syenite, and four composite shonkinite-syenite bodies. One of the shonkinite-syenite stocks is 6300 ft long. Several hundred relatively thin dikes of these potash-rich rocks range in composition from biotite shonkinite through syenite to granite. Although a few thin fine-grained shonkinite dikes cut the granite, the mafic intrusive bodies generally are the oldest and granitic rocks the youngest. The potash-rich rocks are intruded by east-trending andesitic dikes and are displaced by faults.

Veins of carbonate rock are most abundant in and near the southwest side of the largest shonkinite-sye-

nite body. Most veins are less than 6 ft thick. One mass of carbonate rock near the Sulphide Queen mine is 700 ft in maximum width and 2400 ft long. About 200 veins have been mapped in the district; their aggregate surface area is probably less than one-tenth that of the large carbonate mass.

The carbonate minerals, which make up about 60 percent of the veins and the large carbonate body, are chiefly calcite, dolomite, ankerite, and siderite. Other constituents are barite, bastnaesite, parisite, quartz, and small quantities of crocidolite, biotite, phlogopite, chlorite, muscovite, apatite, hematite, goethite, fluorite, monazite, galena, allanite, cerite, sphene, pyrite, chalcopyrite, tetrahedrite, malachite, azurite, strontianite, cerussite, wulfenite, aragonite, and thorite. The rare-earth oxide content of much of the carbonate rock is 5 to 15 percent; in some local concentrations of bastnaesite the rare-earth oxide content is as high as 40 percent.

The foliation and inclusions in the Sulphide Queen carbonate body, and the discordant contacts between this body and the gneissic wall rocks, show that the carbonate rock was intruded as a mass into its present position. Radioactive determinations on monazite from the Sulphide Queen carbonate body indicate a tentative age of 770 million to 1100 million years (pre-Cambrian), and the potash-rich rocks are at least as old, and thus are of pre-Cambrian age.

Because of structural reasons, as well as the pre-Cambrian age of the monazite, the rare-earth-bearing carbonate rock could not have originated as sedimentary limestone or dolomite of Paleozoic age or through assimilation of sedimentary rocks of Paleozoic age by the parent magma of the potash-rich rocks. It might have had a sedimentary origin in the pre-Cambrian gneissic complex as limestone or evaporite, subse-