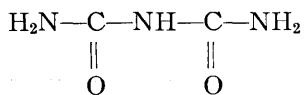

PHENYLBIGUANIDE-*p*-SULFONIC ACID AS AN ANALYTICAL
REAGENT FOR THE COLORIMETRIC DETERMINATION
OF NICKEL

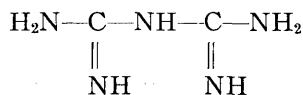
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Chemically and structurally, biguanide is closely related to biuret, for it may be viewed as having been derived from the substitution of both oxygen atoms of biuret by imino (NH) groups.



Biuret

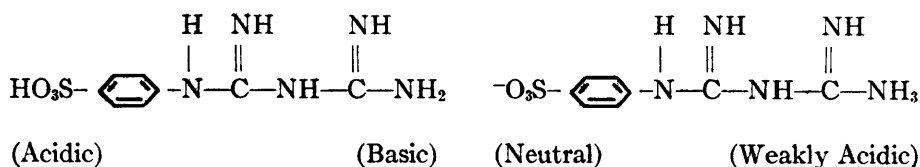


Biguanide

Biguanide and its substituted derivatives have been found to give rise to numerous complexes with many bivalent and trivalent ions of the transitional elements which are characterized by brilliant colors.

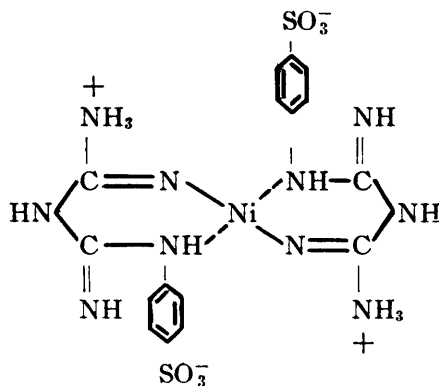
The copper (II), nickel (II), and cobalt (III) chelates of phenylbiguanide-*p*-sulfonic acid have been prepared by Ray and his co-workers and their properties studied (Ray and Siddhanta, 1943). It was, therefore, thought that this ligand should have some use as an analytical reagent for these ions. Experimental investigation showed this to be true.

Phenylbiguanide-p-sulfonic acid exists in the form of a zwitterion, since both the acidic and basic groups are quite strong. The corresponding conjugate basic and acidic groups are respectively neutral and weak.



PHENYLBIGUANIDE-p-SULFONIC ACID

The complexes of this compound are inner metallic compounds and behave as ampholytes (Ray and Siddhanta, 1943). The four-coordinate chelates of copper and nickel are likely to exhibit cis-trans isomerism due to planar configuration (Ray and Chakravarty, 1941). Although variations in preparation were made, the nickel chelate always exhibited the same color, which would indicate only one configuration. From steric considerations it is postulated that the trans form is the stable one (Ray and Siddhanta, 1943).

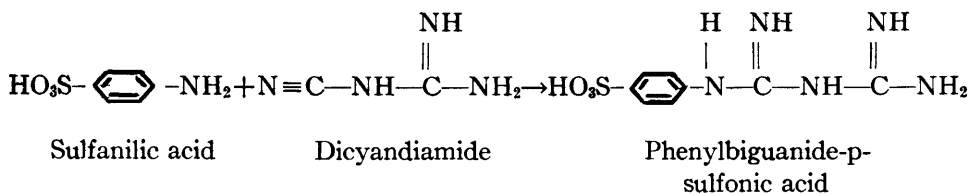


Nickel chelate of phenylbiguanide-p-sulfonic acid

EXPERIMENTAL

Preparation of phenylbiguanide-p-sulfonic acid

This ligand is prepared by the usual reaction for the synthesis of N-substituted biguanides, i.e., the addition of dicyandiamide to an amine.



Preparation of nickel phenylbiguanide-p-sulfonic acid

The compound was prepared by dissolving 1 g of nickel chloride hexahydrate in 100 ml of distilled water. To this solution was added 2.2 g of phenylbiguanide-p-sulfonic acid dissolved in 200 ml of 15 N NH_4OH . The mixture was then heated

for 24 hr at 90°C after which a yellow-orange precipitate was formed. It was then filtered, washed and dried.

Since there was a distinctive color change from blue to yellow by nickel solutions in the presence of the ligand in 15 N NH_4OH , it was felt that this might be the basis of a colorimetric procedure for a quantitative determination of nickel.

Preparation of a standard curve

A series of standard nickel solutions was prepared from nickel (II) ammonium sulfate. To a solution which contained 10, 100, and 1000 ppm NiO, 25-ml aliquots of the ammoniacal reagent were added, boiled for 10 min, cooled and placed in a 50-ml volumetric flask. A spectral distribution curve was run using 50-mm cells in a Beckman DU spectrophotometer. A maximum absorbance was read at 425 μ .

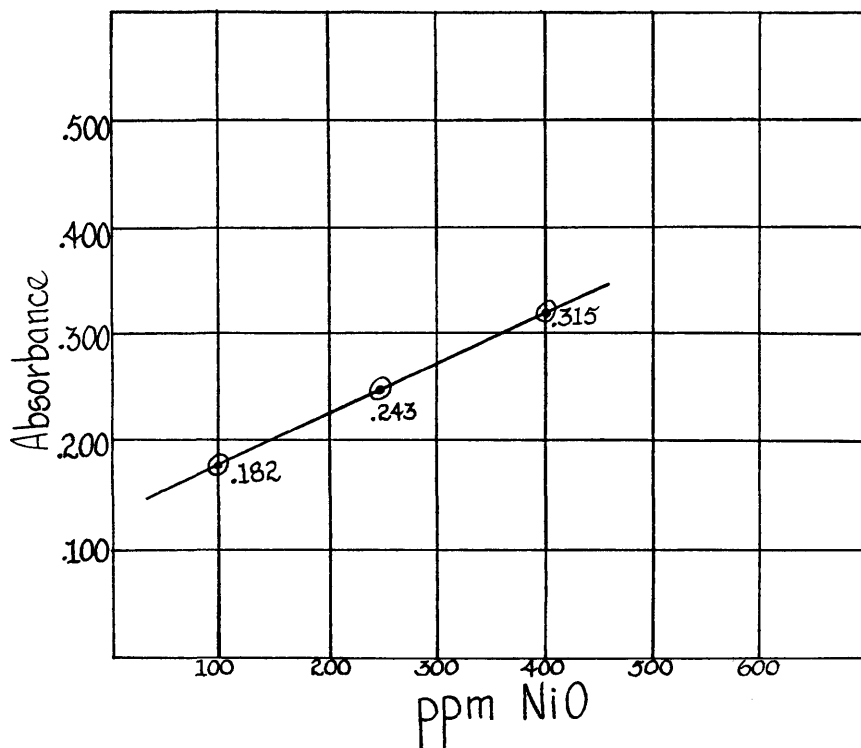


FIGURE 1. Standard curve for nickel ammonium sulfate plus phenylbiguanide-p-sulfonic acid.

To check Beer's Law, 25-ml aliquots of solutions containing 100, 250 and 400 ppm NiO were placed in 150-ml beakers and 25 ml of the biguanide reagent (0.100g/100 ml 15 N NH_4OH) was added to each beaker. The solutions were boiled for 1 min, cooled and transferred to 50-ml volumetric flasks. These solutions were then transferred to the Beckman DU and their absorbances read at 425 μ . Figure 1 shows the adherence to Beer's Law.

Because this method seemed to hold some promise, it was decided to attempt an adaptation of it for the determination of nickel in low-alloy steels. Since, however, the biguanide reagent is dissolved in NH_4OH , the hydrous oxides of iron and other metals present would certainly preclude any direct analysis for nickel. To overcome this difficulty an extraction procedure using dimethylglyoxime in

ethanol was evolved. This extraction method is based on procedures outlined in "Colorimetric Determination of Trace Metals" (Sandell, 1959).

To set up a working curve for the analysis of steels, the low-alloy N.B.S. 16c steel sample was used. This alloy contained 0.023 percent nickel. A 1-g sample of the steel was dissolved in an acid mixture composed of 13.5 ml of concentrated H_2SO_4 and 16.5 ml of 85 percent H_3PO_4 in 100 ml of water. The carbon was removed by boiling with 20 ml of 1:1 HNO_3 until the solution was colorless. After cooling, the solution was placed in a 100-ml volumetric flask. The working curve was prepared by adding 0.0 ppm Ni, 1.17 ppm Ni, and 3.12 ppm Ni to separate 10-ml aliquots of the N.B.S. 16c sample. This was accomplished by adding 3 ml of a 97.5 ppm Ni solution for the 1.17 ppm Ni and 8 ml of the Ni standard for the 3.12 ppm Ni. The standard of 97.5 ppm Ni was prepared from 2.0243 g of $NiCl_2 \cdot 6H_2O$ which was dissolved and diluted to 500 ml. This theoretically would produce a solution of 1000 ppm Ni, but upon gravimetric analysis using dimethylglyoxime, the solution showed only 975 ppm Ni.

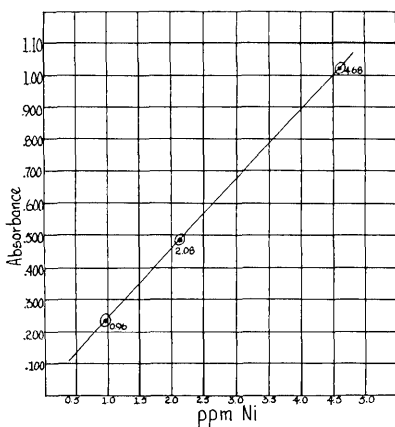


FIGURE 2. Working curve for steel samples. Low range.

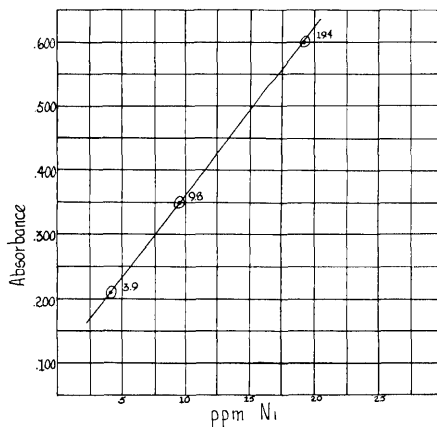


FIGURE 3. Working curve for steel samples. High range.

The nickel was then extracted from the standard steel samples according to Sandell. This entailed an extraction of the dimethylglyoxime chelate with chloroform. The nickel was eventually put back into the aqueous phase by shaking for 0.5 min with successive 15-ml and 10-ml portions of 0.5 N HCl. The 25 ml of the acidic nickel solution was placed in a 50-ml volumetric flask and diluted to the mark with deionized water. The acid solution was now ready for color development.

A 20-ml aliquot of the nickel solution was pipetted into a 100-ml volumetric flask. To this solution a 25-ml portion of the biguanide reagent was added and the solution diluted to 100 ml and allowed to stand for 10 min. A distinctive yellow color was developed at a pH of 11.4 to 11.7.

The absorbance of the various solutions were then measured in the Beckman DU at 380 $m\mu$ using a slit width of 0.08 mm in 50-mm cells. The data obtained are shown in figure 2.

The data obtained for a set of standards which ran from 4 ppm to 20 ppm are shown in figure 3. In this case, 10-mm cells were used and the slit width was set at 0.04 mm.

Using the above outlined procedure, four low-alloy steels obtained from the

Electric Autolite Laboratories, Toledo, Ohio, and a N.B.S. 4g sample were analyzed for nickel. A summary of the results can be seen in table 1.

TABLE 1
Determination of nickel in standard steel samples using phenylbiguanide-p-sulfonic acid

Sample number	% Ni known	% Ni found*
1.	0.16	0.16
2.	0.52	0.53
3.	0.12	0.08
4.	1.17	1.16
N.B.S. 4g	0.065	0.065

*Average of triplicate samples.

In conclusion we feel that this method offers a wide latitude in the amount of nickel which can be determined since the method appears quantitative from 0 to 20 ppm. Therefore, with the proper choice of sample weight and dilution, even high nickel-containing alloys could be analyzed by this procedure.

REFERENCES

- Ray, P., and K. Chakravarty.** 1941. Complex compounds of biguanide with bivalent metals III. Copper and nickel phenylbiguanides and their different modifications. *J. Indian Chem. Soc.* 18: 609.
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