

Figgis B N & Nyholm R S. A convenient solid for calibration of the Gouy magnetic susceptibility apparatus. *J. Chem. Soc.* 1958:4190-1.
[William Ramsay and Ralph Forster Laboratories, University College London, London, England]

The magnetic susceptibility of mercury cobalt thiocyanate, $\text{HgCo}(\text{NCS})_4$, was determined by the Gouy method, as accurately as the method allows. The substance has properties which make it particularly suitable as a calibrant for Gouy equipment used in connection with transition metal complexes. [The SCI® indicates that this paper has been cited over 435 times since 1961.]

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"As a research student beginning to study the magnetochemistry of transition metal complexes, I was advised by Nyholm to use $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a standard to calibrate my newly assembled Gouy magnetic balance. The Gouy balance is very widely used in that field to measure magnetic susceptibility, as it is so easily assembled and robust. On the other hand, it is well known that, owing to the form of the sample, the accuracy obtained with it is quite limited.

"Initial enthusiasm led me to carry out measurements with more care than was necessary for the purposes for which the results were required. It became obvious that the accurately known magnetic susceptibilities for certain materials could not be reproduced upon the basis of the value for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ accepted by magnetochemists. That value was essentially the mean of a rather scattered set of results from the literature.

" $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ could obviously be improved upon as a calibrant. The materials with which I had compared results (e.g., Hg, Cu, Ag) were rather awkward to use in the Gouy method, and were not readily available in high purity, and also, having small

negative susceptibilities, they required unusually good equipment to be compared accurately with the large positive susceptibilities common for transition metal complexes. Perusal of the literature suggested nothing of known susceptibility that seemed ideal. Nyholm suggested we look for the ideal substance and measure its susceptibility by the Gouy method as accurately as possible. In that way a calibrant especially suitable for making comparisons by the Gouy method for transition metal complexes would be obtained.

"Mercury cobalt thiocyanate, $\text{HgCo}(\text{NCS})_4$, was chosen because it is easily prepared in high purity, in the form of fine crystals which pack very well into the Gouy sample tube. It has moderately large magnetic susceptibility, it is suitable for comparisons with other transition metal compounds, and it is chemically very stable and unaffected by the atmosphere. The measurement was performed on a Gouy balance especially constructed for the purpose to optimise accuracy, and employed a very large sample. Water was used as the primary reference material, as its susceptibility had been determined very accurately.¹ The measurement developed into an exercise in tedium, with repeated repacking of the sample tube with products from different preparations to evaluate and reduce errors.

"The paper produced passed the refereeing stage and was published without a hitch. It has been referenced so frequently because the compound involved has become the calibrant of choice for magnetochemistry of transition metal complexes. A confusing sideline to the paper developed because, owing to the exigencies of the refereeing stage, our earlier work on the same compound, which included temperature dependence although presenting a less accurate result for the susceptibility,² appeared after the present paper. A more recent paper³ reviews the various determinations of the susceptibility of the compound and its temperature variation."

1. Piccard A & Devaud A. Nouvelle détermination du coefficient d'aimantation de l'eau. *Arch. Sci. Phys. Nat.* 2:455-85, 1920.
2. Figgis B N & Nyholm R S. Magnetochemistry. Part II. The temperature-dependence of the magnetic susceptibility of bivalent cobalt compounds. *J. Chem. Soc.* 1959:338-45.
3. Bünzli J C G. Comment of the use of $\text{HgCo}(\text{NCS})_4$ as susceptibility standard. *Inorg. Chim. Acta* 36:L413-L414, 1979.