

TABLE 1 — EFFECT OF DIVERSE ION ON THE EXTRACTION OF Pd(II)

{Pd(II) = 100 μ g; pH 1.0; [HMMCO] = 0.002M in isobutanol}

Diverse ion	Added as	Tolerance limit (μ g)
Ag ⁺	AgNO ₃	1500
Al ³⁺	Al ₂ (SO ₄) ₃ ·16H ₂ O	2000
Cd ²⁺	3CdSO ₄ ·8H ₂ O	6000
Co ²⁺	CoSO ₄ ·7H ₂ O	10000
Cr ³⁺	K ₂ SO ₄ ·Cr ₂ (SO ₄) ₃ ·24H ₂ O	600
Cu ²⁺	CuSO ₄ ·5H ₂ O	12500
Fe ²⁺	FeSO ₄ ·7H ₂ O	6200
Fe ³⁺	(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O	3000*
Ga ³⁺	Ga(NO ₃) ₃ ·8H ₂ O	2500
Hg ²⁺	HgCl ₂	20000
In ³⁺	In(NO ₃) ₃ ·5H ₂ O	550
Mn ²⁺	MnCl ₂ ·4H ₂ O	1000
Ni ²⁺	NiSO ₄ ·6H ₂ O	9000
Rh ³⁺	RhCl ₃ ·3H ₂ O	300
Ru ²⁺	RuCl ₃ ·3H ₂ O	None
Tl ⁺	TlNO ₃	1600
VO ²⁺	VOSO ₄ ·H ₂ O	5000
Zn ²⁺	ZnSO ₄ ·7H ₂ O	8000
ZrO ²⁺	ZrOCl ₂ ·8H ₂ O	None
F ⁻	NaF	2000
B ₄ O ₇ ²⁻	Na ₂ B ₄ O ₇ ·10H ₂ O	11000
Mo ₇ O ₂₄ ⁶⁻	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	1200
WO ₄ ²⁻	Na ₂ WO ₄ ·2H ₂ O	3000
PO ₄ ³⁻	KH ₂ PO ₄	5000
SCN ⁻	KSCN	5000
C ₂ O ₄ ²⁻	H ₂ C ₂ O ₄ ·2H ₂ O	2500
Tart ³⁻	Tartaric acid	2000
Cit ³⁻	Citric acid	60
EDTA ⁴⁻	EDTA (disodium salt)	None

*Masked with calculated amount of EDTA (disodium salt).

been found to be $\pm 1.0\%$ and 1.1% respectively. The total operation requires 30 min. Thus, the method is simple, rapid, applicable at tracer concentrations and affords clear-cut separation of Pd(II) from large number of ions.

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References

1. DESHMUKH, B. K., VYAS, C. N. & KHARAT, R. B., *J. Indian chem. Soc.* **52** (1973), 385.
2. NIELSCH, W., *Z. analyt. Chem.*, **142** (1954), 30.
3. SCHLENSKAYA, V. I. & RASHEVSKAYA, A. I., *Chem. Abstr.*, **48** (1954), 13529i.
4. BHATKI, K. S. & RANE, A. T., *Solvent. extr. Chem. Proc. Int. Conf. Göteborg, (1967)*, 147.
5. BANKS, C. V. & SMITH, R. V., *Anal. chim. Acta*, **21** (1959), 308.
6. SOLOWAY, S., *Chem. Abstr.*, **54** (1960), 3895f.
7. DE, A. K., KHOPKAR, S. M. & CHALMERS, R. A., *Solvent extraction of metals* (Von Nostrand, London), 1970, 100.
8. BORKHADE, K. T., *Synthesis of nitrogen and oxygen heterocyclic compounds*, Ph.D. thesis, Nagpur University, 1972.
9. VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longmans, Green, London), 1968, 511.

Direct Determination of Fe(II) with 8-Hydroxy-7-nitrosoquinoline-5-sulphonic Acid

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The title compound has been employed for the rapid, sensitive and selective determination of Fe(II). Interference studies suggest that present method is potentially useful for the determination of Fe(II) in various environmental constituents. Iron has been determined in tap water.

THE well-known amongst the spectrophotometric methods for the direct determination of Fe(II) are those which employ 1,10-phenanthroline¹ and thiocyanate² as complexing agents. In both the methods interferences are observed from various ions commonly associated with Fe(II) including Cu(II) and Ni(II). The 1,10-phenanthroline method which is more sensitive amongst the two ($\epsilon = 1.1 \times 10^4$ at 505 m μ) requires longer time for maximum colour development. Methods of equal or higher sensitivity which are based on extractive determination, viz. those employing 2-nitroso-1-naphthol³, dithiazone⁴, diethyldithiocarbamate⁵ and cupferron⁶ likewise suffer from limited selectivity and complications during colour development. The present method employing the disodium salt of 8-hydroxy-7-nitroso-quinoline-5-sulphonic acid (NHQS) is highly selective, sensitive ($\epsilon = 1.85 \times 10^4$) and extremely rapid.

With Fe(II), NHQS rapidly forms a bright green complex at pH 3.5-6. Complex formation takes place at lower pH values also but its rate of formation decreases as the pH is lowered. Several other ions, e.g. Cu(II), Ni(II), UO₂(II), etc., also form complexes with NHQS at this pH range but while the Fe(II)-NHQS system does not disproportionate if the acidity of the system is lowered below pH ≈ 0.5 , other complexes readily breakdown. This phenomena has been utilized for the selective determination of Fe(II).

Deionized water was used for all purposes. All other chemicals were reagent grade unless specified. Standard solutions of Fe(II) and other metal ions were prepared by standard methods⁷. A Perkin-Elmer 492-5000 spectrophotometer was used for recording absorption spectra. Measurements at a constant wavelength were done with a SF-4 (USSR) spectrophotometer using matched quartz cells.

The reagent NHQS was prepared by nitrosation of 8-hydroxyquinoline-5-sulphonic acid and subsequent conversion of mono-sodium salt to disodium salt, following the method of Aly *et al.*⁸. Its saturated solution in water was used.

Determination of iron(II)—To 8 ml of acetic acid-sodium acetate buffer solution of pH ≈ 5 , 5 ml reagent solution and 5 ml sample solution containing 0.5×10^{-4} to $5 \times 10^{-4}M$ Fe(II) were added in succession. After standing for 1 min, the mixture was brought to pH ≈ 0 by dropwise addition of conc

HCl, transferred to a 25 ml volumetric flask, made up to the mark and measured spectrophotometrically at 705 nm against a reagent blank prepared in a likewise manner.

The reagent has a negligible absorption at 705 nm. In the absence of interfering ions, a $1 \times 10^{-3} M$ reagent solution is adequate for complete colour development with Fe(II). In the presence of high concentration of foreign ions, a saturated reagent solution should be used.

The green complex obeys Beer's law in the range 0.2-5.6 $\mu\text{g/ml}$ of Fe(II), the molar absorptivity and Sandell sensitivity⁹ at λ_{max} (705 nm) being 1.8×10^4 litre mole⁻¹ cm⁻¹ and 0.003 μg of Fe(II) cm⁻² respectively. The colour is stable indefinitely at pH 4.5-6 but once it is made highly acidic, it begins to fade slowly. The absorbance measurements should, therefore, be made within 30 min of the acidification of the sample-NHQS system.

The ions commonly associated with Fe(II) in natural or synthetic mixtures, viz. Al(III), Cu(II), Ni(II), Zn(II), Mn(II), Hg(II), Cd(II), Mg(II), Be(II), Cr(VI), UO₂(II), Ca(II), Na(I), K(I), are tolerated in ratios 1:100: Fe(II): foreign ion. Presence of SO₄²⁻, NO₃⁻, CH₃COO⁻, Cl⁻, Br⁻, I⁻ has no effect on the determination. Complexing ions citrate, tartarate, ascorbate and thiosulphate are tolerated in ratios 1:1000. Gold(III), V(IV), Ce(III), Th(IV), La(III) and Ti(IV) are tolerated if present in concentrations 25 times to that of Fe(II) while Pt(IV), Ru(III), Os(III), Pd(II), Ag(I) and Co(II) can be present in a concentration comparable to that of Fe(II). Attempts to mask Co(II) with citrate, tartarate, thiosulphate and nitrite were unsuccessful.

Determination of Fe(II) in tap water — Tap water (2 litres) was concentrated to 5 ml by boiling. After cooling, it was brought to pH ≈ 4 with HCl and 2 ml of 1% hydroquinone solution was added to it to reduce Fe(III) to Fe(II). From this solution, Fe(II) was determined as described before. Quadruplicate measurements yielded a value 0.84 ± 0.02 ppm.

Composition of the complex — Aly *et al.*⁸ had proposed that in Fe-NHQS system Fe(II) is chelated to the oxygens of nitroso and hydroxyl groups of the ligand. The unpublished kinetic and potentiometric studies of the present workers endorse this view and confirm that in the green complex, Fe and NHQS are combined in a ratio 1:3.

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References

- MARGERUM, D. W. & BANKS, C. V., *Analyt. Chem.*, **26** (1954), 200.
- CHARLOT, G., *Colorimetric determination of elements* (Elsevier, New York), 1964, 272.
- GORBACH, G. & POHL, F., *Mikrochimie mikrochem. Acta*, **38** (1951), 258.
- DAWSON, E. C., *Analyst*, **73** (1948), 618.
- CHALMERS, R. A. & DICK, D. M., *Analytica chim. Acta*, **31** (1964), 520.
- DE, A. K., KHOPKAR, S. M. & CHALMERS, R. A., *Solvent extraction of metals* (Van Nostrand, New York), 1970.

- SKOOG, D. A. & WEST, D. M., *Analytical chemistry* (Holt, Rinehart & Winston, New York), 1963, 457.
- ALY, M. M., MIKHAYAN, M. & EL-EZABY, S., *J. inorg. nucl. Chem.*, **35** (1973).
- SANDELL, E. B., *Colorimetric determination of traces of metals* (Interscience, New York), 1959.

Hexacyanoferrate(III) as a Primary Standard for the Determination of Sb(III) in Bicarbonate Medium

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Arsenic(III) and antimony(III) in bicarbonate medium can be determined using hexacyanoferrate(III). The method involves liberation of iodine from potassium iodide by ferricyanide in the presence of zinc sulphate and titration of this iodine with As(III) or Sb(III).

SEVERAL methods, such as gravimetric¹, amperometric², potentiometric³, spectrophotometric⁴ and titrimetric, are available for the determination of As(III) and Sb(III). Amongst the various titrimetric methods⁵⁻¹⁴ indirect cerimetric method¹² in acid medium and chloramine-T method⁶ in alkaline medium, appear to be most suitable. In the iodine method¹⁰, which is simple and is applicable in bicarbonate medium, iodine is not a primary standard. Other methods of determination are either not direct or not easy to manipulate. Recently silver(III)¹⁵, copper(III)¹⁶ and N-bromosuccinimide¹⁷ have also been reported to react with As(III). It has been found by Deshmukh and Sant¹⁸ that hexacyanoferrate(III) can be employed for the determination of As(III) in bicarbonate medium. In the present note an improvement over this method has been suggested. It is found that KI can be added directly in the bicarbonate medium and that there is no necessity of adding HCl. The determination of Sb(III) is also described.

Potassium hexacyanoferrate(III), zinc sulphate, sodium bicarbonate and potassium iodide were of BDH (AnalaR) quality. Sodium metaarsenite (Riedel) was employed as source of As(III) and potassium antimonyl tartrate (May & Baker) for Sb(III). Solutions were prepared by direct weighing in redistilled water (second distillation from permanganate). Aqueous solutions of As₂O₃ obtained by boiling it with water and acid solutions of Sb₂O₃ obtained by boiling it with 30% perchloric acid, could also be used. Alkaline solutions of As(III) after neutralizing it with HCl could also be used. These solutions were standardized iodometrically¹⁰.

Procedure — Hexacyanoferrate(III) solution (2-10 ml) of suitable concentration, saturated solution of sodium bicarbonate (5 ml) and potassium iodide (2 g) were taken in an Erlenmeyer flask and the volume made up to 25 ml. 0.2M ZnSO₄ solution (5 ml) was added with shaking. The liberated iodine was titrated against the unknown As(III) or Sb(III)