

TABLE 2—ESTIMATION OF Fe(II) AND U(IV) WITH VANADATE OR CERIC SULPHATE

Fe(II), mg		Error (%)	U(IV), mg		Error (%)
Taken	Found		Taken	Found	
SODIUM VANADATE					
28.80	28.70	-0.3474	20.80	20.73	-0.3365
40.30	40.20	-0.2484	11.10	11.13	+0.2703
51.80	51.65	-0.2896	5.25	5.26	+0.1908
5.90	5.92	+0.3389	33.70	33.60	-0.2967
12.48	12.52	+0.3204	27.68	27.60	-0.2890
CERIC SULPHATE					
5.70	5.68	-0.3508	37.50	37.60	+0.2667
10.60	10.63	+0.2830	26.20	26.12	-0.3053
17.10	17.04	-0.3509	17.12	17.18	+0.3405
23.50	23.44	-0.2553	11.40	11.37	-0.2631
28.75	28.83	+0.2783	2.93	2.924	-0.2047

V(III) interferes in the estimation of Fe(II) with vanadate in sulphuric acid medium, whereas it does not interfere in the present case. Oxalate, As(III) and U(IV) interfere in the estimation of Fe(II) with ceric sulphate in sulphuric acid medium, but in the present case they do not interfere.

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Extraction & Spectrophotometric Determination of Pd(II) with 2'-Hydroxy-4-methoxy-5'-methylchalkone Oxime

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A fast and selective procedure is described for the extraction and direct spectrophotometric determination of Pd(II) using 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) in isobutanol. The Pd(II)-HMMCO complex is quantitatively extracted at pH 0.5-2.5 and obeys Beer's law in the concentration range 1.0-30.0 μg of Pd(II) per ml of isobutanol at 380 nm. The complex having molar absorptivity 3.38×10^3 is highly stable. Palladium can be clearly separated and determined in the presence of large number of ions.

THE use of 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) for the simultaneous gravimetric determination of Pd(II), Cu(II) and Ni(II) has been described by us earlier¹. The study of liquid-liquid extraction of less common metals in our laboratory showed that Pd(II) can be quantitatively extracted with HMMCO in the pH range 0.5-2.5. This has now been employed for the spectrophotometric determination of Pd(II).

The extraction of Pd(II) with several oximes are known²⁻⁶. Amongst many oximes the quantitative extraction with resacetophenone oxime⁴ required 5 hr whereas with the present oxime it takes 8-10 min for quantitative extraction. In addition a number of other chelating agents⁷ were also tried as extractants.

The oxime was synthesized from *p*-cresol as reported earlier⁸. About 0.002M HMMCO in isobutanol was used for extraction studies.

A stock solution of palladium perchlorate was prepared by dissolving palladium chloride (~ 0.98 g, Johnson-Matthey) and standardized by gravimetric methods^{1,9}. The solutions of desired concentrations were prepared by appropriate dilution.

General procedure—The pH of a solution containing 100 μg of Pd(II) was adjusted 1.0-2.0 with perchloric acid and sodium hydroxide, the final volume being 25 ml. The solution was shaken with 10 ml of 0.002M HMMCO in isobutanol for 10 min. The organic layer was separated and the absorbance was measured at 380 nm, the wavelength of maximum absorbance, against the reagent blank. Pd(II) present was computed from the calibration curve, as usual.

The molar absorptivity of the complex was 3.38×10^3 . The sensitivity by Sandell's definition is 0.020 $\mu\text{g}/\text{cm}^2$. The Pd(II)-HMMCO system obeyed Beer's law over the concentration range 1-30 μg of Pd(II) per ml of isobutanol. Most suitable working range according to Ringbom plot was found to be 10-20 μg of Pd(II) per ml of isobutanol. Pd(II)-HMMCO complex is stable for 5 days.

The quantitative extraction of Pd(II) is possible with reagent concentration 2×10^{-3} - 2.5×10^{-3} M over the pH range of 0.5-2.5. The extraction decreases above pH 3.0 for all concentration of the reagent.

The composition of the extractable species was found to be 1:2 (Pd-HMMCO) by the plot of $\log D_{\text{Pd}}$ versus $\log C$ (HMMCO concentration).

Amongst the various non-aqueous solvents, viz. methyl isobutyl ketone, *n*-butanol, isoamyl alcohol, cyclohexanol, ethyl acetate, chloroform and benzene, isoamyl or isobutyl alcohol were found to be most efficient.

Many foreign ions were tested for interferences. The tolerance limit was set as the amount of foreign ion needed to cause $\pm 2\%$ error in the recovery of Pd(II). Many ions are tolerable whose tolerance limit are given in Table 1. The tolerance of Hg(II) is hundred and fifty-fold, whereas that of Rh(III) is three-fold. The strong interfering ions include Fe(III), Ru(III), ZrO(II), citrate, tartarate and EDTA.

The absorbance obtained from eight determination of 100 μg of Pd(II) was 0.500 ± 0.005 . The relative mean deviation and standard deviation have

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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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