TABLE II

Effect of various acids on the absorbance

$[Mo (VI)] = 1 \cdot 6 \times 10^{-3}$ M

$[Acid] = 4 \times 10^{-3}$ M

$[Oxime] = 4 \times 10^{-3}$ M

Acid	Absorbance
HCl	0·39
H_2SO_4	0·29
$HClO_4$	0·31
HNO_3	0·18
H_3PO_4	Very little
CH_3COOH	0·27
$CH_3 \cdot CH_2 \cdot COOH$	0·24

calculated using the data obtained in Job's method is 1×10^4.

Effect of Diverse Ions.—It was found that K^+, Na^+ Cl^-, NO_3^-, $SO_4^=$, I^- did not interfere and oxalate, tartrate, citrate, phosphate; borate, acetate, EDTA, Fe^{3+} and Al^{3+} interfered. W^{6+}, V^{5+} and V^{4+} interfere when their respective concentrations exceed 184, 1·5 and 15 ppm. Cr^{3+} and fluoride interfere if the amount exceeds 1·5 and 150 ppm respectively. Fe^{3+} (< 18 ppm) is successfully maked by the addition of fluoride (> 150 ppm). Higher amounts of Fe^{3+} can effectively be masked by potassium iodide and the iodine liberated is removed by adding the just sufficient amount of sodium thiosulphate solution. A 40 fold excess of Zn^{2+}, Mn^{2+}, Cd^{2+}, and Ni^{2+} do not interfere.

The present method can therefore be employed for the analysis of molybdenum in high speed and alloy steels.

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A SPECIFIC SPOT TEST FOR PALLADIUM USING DIPHENYLDISULPHIDE 2:2'-DICARBOXYLIC ACID

DURING the course of our studies on the reactions of thio-salicylic acid with metal ions, it was observed that the oxidised product of this compound, *viz.*, diphenyldisulpride 2 : 2'-dicarboxylic acid yielded a color reaction with palladium but not with other metal ions. Since the reagent is easy to prepare and the reaction is found to be highly specific for palladium, its potentialities as a spot test reagent for palladium were investigated.

Experimental—Reagents :

Palladium chloride solution : Palladium chloride solution (1 ml $\approx$ 0·5 mg) was prepared using Johnson & Matthey sample. The strength of the solution was ascertained gravimetrically using dimethylglyoxime[1]. More dilute solutions were prepared from this stock solution.

Diphenyldisulphide 2:2'—dicarboxylic acid solution : (a) This reagent could be prepared starting from o-amino benzoic acid and sodium disulphide[2]. A 0·1% (W/V) solution in absolute alcohol was used. (b) The reagent could be more conveniently prepared starting from thiosalicylic acid as follows :

Thiosaliclic acid silution, in alcohol (5 ml of 1%) was taken in a centrifuge tube and treated with hydrogen peroxide. A white precipitate separated out. It was then centrifuged, the precipitate washed thrice with alcohol (5 ml each time) and again shaken up with alcohol to obtain the saturated solution of the reagent. The solubility of the reagent in absolute alcohol was about 150 mg per 100 ml of alcohol.

Procedure : A drop (0·04 ml) of the palladium chloride solution which is not more than 0·05 M with respect to hydrochloric acid (but of any concentration with respect to other mineral acids) is placed on a spot plate and treated with a drop of the reagent solution.

An orange red to red color develops depending upon the amount of palladium.

Limit of identification $= 0 \cdot 8\ \gamma$
Dilution limit $= 1 : 50,000$

Effect of foreign ions:

The influence of many cations and anions was studied by preparing solutions such that each drop contained $0 \cdot 8\ \gamma$ of palladium and varying amounts of foreign ion. Since the usual process of bringing palladium into solution results in the chlorides of metals, the foreign metals added were in the form of chlorides except in cases where their low solubilities prevented their use. The tolerance limits of various foreign ions are given in Table 1. It is interesting

TABLE I

Tolerance limits of foreign ions

Palladium present in one drop $(0 \cdot 04\ ml) = 0 \cdot 8\ \gamma$

Cation	Tolerance limit, mg	Anion	Tolerance limit, mg
Au (III)	0·5		
Pt (IV)	0·5	Chloride	3·0
Rh (III)	0·16	Bromide	1·6
Ag (I)	10·0	Iodide	3·2
Te (IV)	2·0	Fluoride	5·0
Mn (II)	5·0	Cyanide	0·004
Co (II)	5·0	Oxalate	0·05
Ni (II)	1·6	Tartrate	2·0
U (VI)	0·8	EDTA	0·2
Cu (II)	3·2	Sulphate	all concentrations
Zn (II)	2·5	Nitrate	all concentrations
Fe (III)	5·0		
NH₄ (I)	2·5		
Pb (II)	10·0		
Mo (VI)	2·5		
Ca (II)	2·5		
Mg (II)	2·0		
Tl (I)	5·0		
Al (III)	3·0		
Be (II)	2·5		
Ti (IV)	3·0		
Hg (II)	1·5		

to observe that chloride ion exerted a limiting effect on the color reaction. But for this, the tolerance limits of several metal ions would have been several times more. For example, the tolerance limit of Mg^{++} ion when added in the form of chloride was 2 mg/$0 \cdot 8\ \gamma$ Pd, whereas it was found that even 10 mg of it could be tolerated when the same was added in the form of nitrate. Similarly the color development was inhibited when the hydrochloric acid concentration was greater than $0 \cdot 1M$ whereas the reaction was even more sensitive in the presence of sulphuric, nitric, perchloric and acetic acids at all concentrations. Hence in presence of excess hydrochloric acid or metal chlorides, the solution can be evaporated to near dryness in a microbeaker with one or two drops of concentrated sulphuric acid over hot water bath. The residue, after dissolving in the minimum amount of water, can be tested for palladium. Conversion of chlorides to sulphates is very smooth in the case of several base metals. This incidentally helped in overcoming the difficulty in observing the color change due to palladium in the presence of colored salts such as iron (III) chloride. Iron (III) also gave a color reaction when the acid concentration was as low as $0 \cdot 01$ M. But this reaction was suppressed by either slightly increasing the acidity or by the addition of a drop of 1% potassium bifluoride solution.

Several spot tests are reported for palladium based on color development with organic reagents as well as catalytic action of palladium. Among these, the spot test involving the use of dimethyglyoxime (identification limit: $0 \cdot 05\ \gamma$) is popular[3]. But this spot test is based on the protective action of palladium complex over the red nickel complex and this is responsible for the high sensitivity. However, the direct interaction of palladium and dimethylglyoxime yielding an yellow colored precipitate is not as sensitive as with the present reagent. Moreover, gold does not interfere with the present reagent.

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