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STUDY OF THE OXIDATION OF PLATINUM (II) WITH HEXAMINECOBALT (III) TRICARBONATOCOBALTATE (III)

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A number of volumetric and gravimetric methods for the determination of platinum are reported in literature.[1] Gravimetric methods depend largely upon the formation of the most characteristic platinum compound $(NH_4)_2$ Pt Cl_6 which is reduced to the platinum metal on heating and then estimated, while volumetric methods are based upon the fact that platinum is reduced to the bivalent state by a variety of substances and then titrated against some oxidant.[2-5]

In previous investigation[6-12] we have successfully utilized the strong oxidizing power of hexaminecobalt (III) tricarbonatocobaltate (III) for the determination of a number of compounds using ferroin as indicator. In order to extend its scope in volumetric analysis we have tried to devise a method for the determination of platinum and results of this study are reported here.

Experimental

Reagents : (i) Hexaminecobalt (III) tricarbonatocobaltate (III). Its solution was prepared and the factor was checked according to the method described earlier.[6]

(ii) Chloroplatinic acid ($H_2Pt\ Cl_6\ 6H_2O$). An appropriate solution was prepared by dissolving 155 mg/ml of the substance (Peking Chemical Works, China) in 5N hydrochloric acid and after its reduction to bivalent platinum with copper (I), the factor was checked agaist standard potassium permanganate.[4] Exact dilutions of this stock solution were made for preparing solutions of low concentrations.

(iii) Ferroin. The M/40 solution (Fluka) was used as the indicator.

All the other reagents used were of analytical grade or of equivalent purity unless mentioned otherwise.

Procedure. A definite aliquot of the platinum (II) solution containing 154.68 μg-24.88 mg was taken in a flask to which water and sulphuric acid were also added to get a 20 ml total volume which was 8N with respect to H_2SO_4. This was titrated against standard hexaminecobalt (III) tricarbonatocobaltate (III) using ferroin as indicator. The end point was detected by the change of red colour to pale blue. Blank titration was run and the actual volume of the titrant used for the test solution was obatined after deducting the blank from the total.

Calculation. Amount of platinum (mg)=N×V×E, where N=normality of the titrant,

V=volume of the titrant used for the titre.

E=equivalent weight of platinum (II).

Results and Discussion

As evident from Tables 1-2 platinum can be determined with hexaminecobalt (III) tricarbonatocobaltate (III) from 154.68 μg-24.88 mg amounts with a maximum error of −2.40%. The reaction between platinum and cobalt proceeds according to the following equation :

$$Pt^{2+} + 2Co^{+3} \longrightarrow Pt^{+4} + 2Co^{2+}$$

According to the above equation, platinum (II) is directly oxidized to platinum (IV) and consequently cobalt (III) is reduced to cobalt (II). The volume consumption of the titrant is a direct proof of the fact.

The reaction proceeds very fast and one titration could be done in about 2-3 min. The end point, i.e. change from red to pale blue, is very sharp and persists for about 3 min ; therefore, it is detected without any difficulty.

TABLE

Pt taken (mg)	Pt found (mg)	Error (%)	Pt taken (μg)	Pt found (μg)	Error (%)
1.56	1.58	+1.93	154.68	151.56	−2.01
2.48	2.50	+0.80	309.36	316.90	−2.40
4.03	4.02	−0.24	464.05	468.46	+0.95
12.44	12.44	±0.00	618.73	620.03	+0.22
20.58	20.59	+0.04	773.41	785.37	+1.54
24.88	24.85	−0.12	928.99	936.93	+0.85

The effect of diverse ions on this determination has been studied. Palladium up to about 4.7 fold in excess to platinum does not interfere in any way with palladium determination while irridium, osmium and gold interfere strongly. The interference of gold can be eliminated by adding a known excess of ethyl acetate to a solution of platinum test solution containing gold. The solution is shaken well after which the ethyl acetate layer is separated with a separating funnel. This is repeated with fresh ethyl acetate and the resulting aqueous solution is titrated against the titrant in the usual manner.[13]

The method reported here is quite simple, precise and accurate.

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THE EFFECT OF SOME SULPHUR FUNGICIDES ON POWDERY MILDEW OF CHILLIES

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Chillies (*Capsicum annuum* L.) occupy about 10,000 hectares in the province of Sind. Their cultivation is often handicapped by the development of powdery mildew caused by *Leveillula taurica* (Lev.) Arnaud. Infections are sometimes so severe that defoliation takes place and yields are reduced appreciably. Veldeyron (1955) estimated a loss of 20-50% in the crop due to premature leaf fall after infection.

No studies so far on the chemical control of powdery mildew of chillies appear to have been made (Patli, 1959; Pucci, 1962). The present investigations were undertaken to test the efficacy of three sulphur fungicides against the powdery mildew of chillies.

Materials and Methods

The experiment was conducted in a 5×5 Latin square design. The size of the unit plot was 9′×9′ accommodating 24 plants at spacings of 27″×18″. Seedlings of the "talhar" variety were transplanted in the second week of July. At the time of natural appearance of the powdery mildew in October all the plants were artificially inoculated with the conidial suspension of *L. taurica* (15-20 conidia/drop). Then the treatments with the respective fungicides, as detailed below, were started and repeated at 15-day intervals. In all, three applications were made. One inoculated plot in each replication was left unsprayed to serve as "untreated control".

Fungicides tested against powdery mildew of chillies were as follows :

Chemical	Form	Dose	Active ingredient	Source
Sulforon	Spray	2 lb/100 gal.	97%elemental sulphur	Dupont
Sulforon	Dust	25 lb/acre	97% elemental sulphur	Dupont
Thiovit	Spray	2 lb/100 gal.	80% micronized sulphur	Sandoz
Cosan	Spray	2 lb/100 gal.	Colloidal wettable sulphur	Ciba

Data were collected on the incidence of powdery mildew on the basis of the infected leaves (Munjal *et al.* 1963) and the yield of fresh red chillies. Angular transformations were made to percentages to bring data to the form of normal distribution for statistical analysis (Clark & Leonard, 1939).

Results

The effects of various treatments on the incidence of powdery mildew and yield of chillies are presented in Tables 1-2 respectively.

TABLE 1. PERCENTAGE INCIDENCE OF POWDERY MILDEW IN VARIOUS TREATMENTS.

Treatments	% incidence of powdery mildew in each year				% reduction in disease over untreated control
	I	II	III	Mean	
Sulforon dust	16.1	14.3	15.2	15.2	32.0
Sulforon spray	21.5	19.8	19.8	20.3	26.8
Cosan	34.7	31.8	29.3	31.9	15.2
Thiovit	30.5	29.7	23.2	27.8	19.2
Untreated control	49.7	48.7	45.0	47.1	—
S. E. of treatment means	** ±1.78	** ±0.97	** ±1.48	** ±0.84	

**Differences between means significant at P= .01.

It is evident from the above results that the fungicides tested significantly lowered the infection of powdery mildew (Table 1) and increased the yield of chillies (Table 2) over untreated control. Best results were obtained with *Sulforon* in dust form which on average basis gave 32 % reduction in disease incidence and 35 per cent higher yield. This was followed by *Thiovit* and *Cosan* which also checked the infection with a corresponding increase in yield.

Discussion

Infections of the powdery mildew of chillies in the province of Sind appear to be as severe as reported by Pucci (1959) and Orieux and Fleix (1963) from other countries. Investigations reported in this paper have indicated that disease incidence can be reduced to a greater extent and the yield of chillies can be improved by the use of sulphur fungicides. However, factors affecting the development of powdery mildew to such an epiphytotic condition need further investigations. These factors may include environmental conditions as well as agrotechniques such as the planting time and finding the source of primary infection.

TABLE 2. EFFECT OF VARIOUS TREATMENTS ON THE YIELD OF CHILLIES.

Treatments	Yields in lbs/Plot each year				% increase in yield over untreated control
	I	II	III	Mean	
Sulforon dust	13.3	13.8	14.2	13.8	35.2
Sulforon spray	11.9	12.9	13.7	12.9	25.2
Cosan	10.8	10.9	12.2	11.3	10.1
Thiovit	12.1	11.5	13.2	12.3	19.7
Untreated control	8.8	10.3	11.7	10.3	—
	**	**	**	**	
S. E. of treatment means.	±2.27	±0.24	±0.19	±0.41	

The causal fungus is reported to attack 40 host plants in Sind (Khan & Kamal, 1968), and thus its strains may be highly specialized in parasitism (Chupp & Sherf, 1960). This shows the importance of studying cross inoculations of strains and hosts, and finding disease-resistant varieties of chillies. Until such factors are studied and a disease-resistant variety is available, the use of promising sulphur fnugicide such as *Sulforon* is necessary to keep powdery mildew infection to the minimum and to obtain substantial increase in the yield of chillies.

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