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Brilliant Green as a Releasing Agent in Atomic Absorption Spectrometric Determination of Rhodium

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In atomic absorption spectrometric determination of rhodium, the interfering effects of different cations and anions can be completely eliminated by addition of excess of brilliant green. Brilliant green has two roles: first, it forms stable complex with the analyte, so that the rhodium species reaching the flame will be normally independent of the original composition of the solution, secondly, the high excess of brilliant green scavenge the oxidizing species in the flame producing favourable condition for rhodium atomization.

INTRODUCTION

In relation with work on the catalytic effect of rhodium complexes and or its metal oxide on silicon dioxide have been of interest. Flame atomic absorption spectrometry (FAAS) was to be used for their analysis. The literature data indicated that many other metal ions and complex forming substances interfer seriously. The use of U or mixture of Cu and Cd and or La could not be applied to the complexes studied[1–5]. In many cases organic ligands, were found effective in elimination of interferences in determination of many analytes[6–8]. However, investigation about the effect of organic addenda in the flame spectrometric determination of Rh is not available in the literature. Moreover, the use of brilliant green (B.G.) as a sensitive spectrometric procedures for determination of many analytes were studied[9–11]. The aim of the present study is to investigate the feasibility of using a continuous titration technique[12] for studying the role of the organic releasing agent (brilliant green) in atomic absorption spectrometric determination of rhodium.

EXPERIMENTAL

A Perkin-Elmer double-beam 2380 atomic absorption spectrometer was used with adapted Unicam rhodium hollow-cathode lamp and conventional 10 cm slot burner head for an air acetylene flame. A continuous titration device[12] was attached to the instrument, absorbance value were recorded with a PM 8251 single-pen recorder. The operating parameters and the instrumental settings were as follows: lamp current, 10 mA; wavelength, 343.5 nm; slit width, 0.7 nm; Air flow rate, 21 L min^{-1}; fuel flow rate, 3 L min^{-1} for burner head 10 cm (1 slot). All the reagents used were of analytical-reagent grade. The solution of the metals investigated were prepared by dilution from (BDH) standard solutions for AAS.

RESULTS AND DISCUSSION

Effects of brilliant green

The effect of brilliant-green on the absorbance of rhodium atoms is shown in Fig. 1, the experiment was conducted using the continuous titration method. In

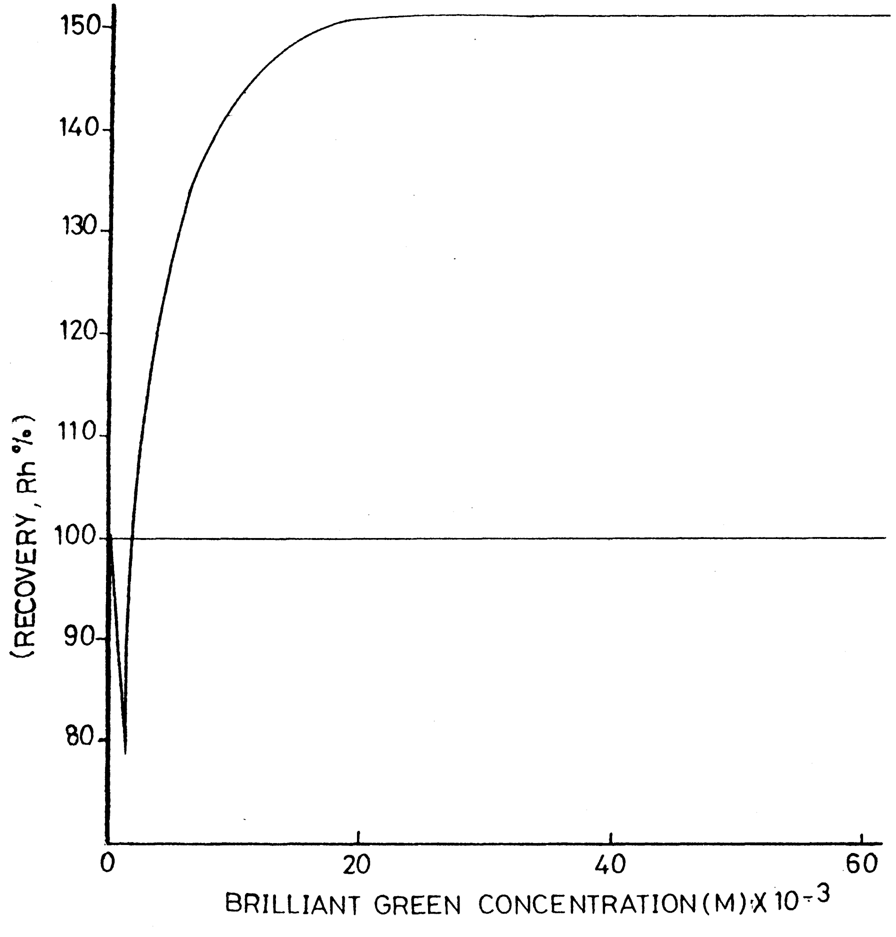

Fig. 1 Changes in the absorption of rhodium as a function of brilliant green concentration. Titration of 1.9 × 10^{-4} M rhodium with brilliant green.

the first stage of the titration, the absorbance signal decreases and finally increases to about 150% recovery when a large (>100 fold) excess of brilliant green was added. For evaluation of the molar ratios at the observed break points, the same

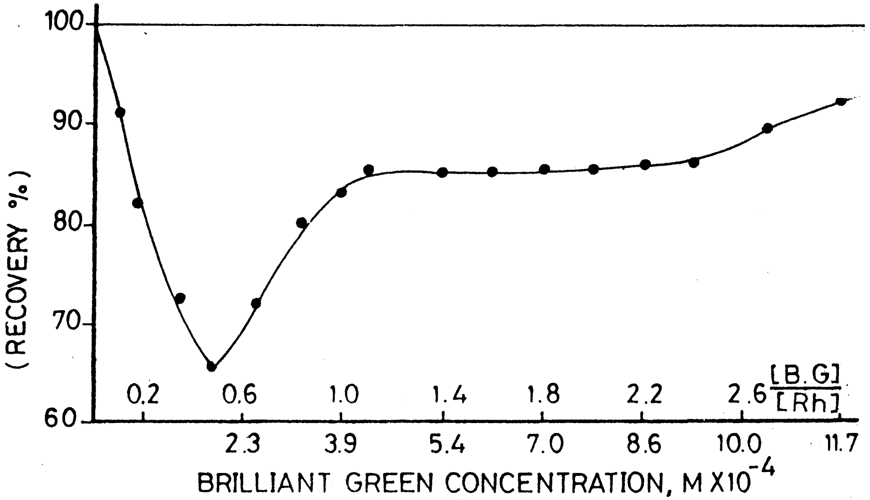

Fig. 2 Changes in the absorption of rhodium as a function of the brilliant green/rhodium green/rhodium ratio. Titration of 9.7×10^{-4} M rhodium with brilliant green.

titration is performed to enlarge the first portion of the titration, the data are depicted in Figure 2. Clearly, brilliant green imposes itself on the atomization process of Rh. It is more likely that, Rh-complexes corresponding to [B,G]/[Rh] molar ratios 1 : 2 and 1 : 1 were formed. It can also be concluded that the reaction between rhodium and brilliant green is completed at 1 : 1 molar ratio and it is more vaporize in the flame than $(Rh)_2$–brilliant–green complex as shown in Figure 2. Increasing the concentration of brilliant green to about 2.5 times rhodium concentration, gradual enhancement on the absorbance was observed, and at very large (>100 fold) excess of brilliant green, the absorbance of rhodium reaches to a saturation state (Fig. 1). Clearly, the excess of brilliant green concentration plays a significant role in the atomization of Rh atoms in the air–acetylene flame. In an attempt to interpret this latter role of brilliant green, a comparison between the effect of increasing amount of ammonium chloride or brilliant green individually on absorption signal of Rh atoms comes from Rh–brilliant green complex. (This complex is prepared by stochiometric addition of Rh–brilliant green (1 : 1) in aqueous solution) as shown in Figure 3. Ammonium chloride should not affect the Rh–brilliant green complex but it vapourise and enhance the disintegration of solid aerosols in the flame, thus increasing the specific surface available for atomization[13,14]. The results of this essentially physical effect is a gradual increase in the signal of rhodium with large amount of amonium chloride.

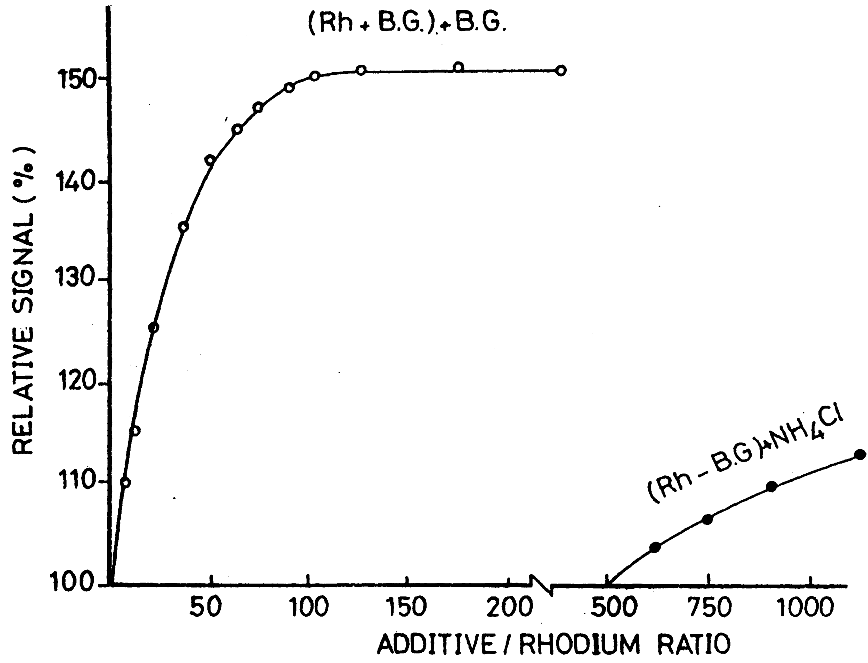

Fig. 3 Changes in the absorption signals of rhodium (Rh-B.G) with increasing ammonium chloride and brilliant green concentration.

In contrast, when brilliant green was added, the absorption raises readily, and attains a saturation level at ratio [B.G]/[Rh] = 100. This comparison may indicate that, the presence of large excess of brilliant green plays a significant effect in the atomization process. The decomposition of organic ligands (large excess of B.G.) enrich the flame with different entities such as, CH, C, H, HCO, . . .[15]. These reducing species may decrease or eliminate the oxygen atoms from the region or measurement according to the following equations:

$$CH + O \rightarrow CO + H$$

$$H + O \rightarrow OH$$

To investigate the validity of this concept, brilliant green of increasing concentrations were aspirated into the flame and the OH and CO emission intensities were recorded. Figure 4, shows increasing of both emission intensities as the brilliant green concentration increase in the flame. Thus increasing the concentration of the brilliant green in air–acetylene flame decrease the oxidizing species, hence, the rhodium atoms in the flame increase and reach a saturation state at large (>100 fold) excess ligand.

Effect of foreign cations

The relationship between the free rhodium atoms population and the height of

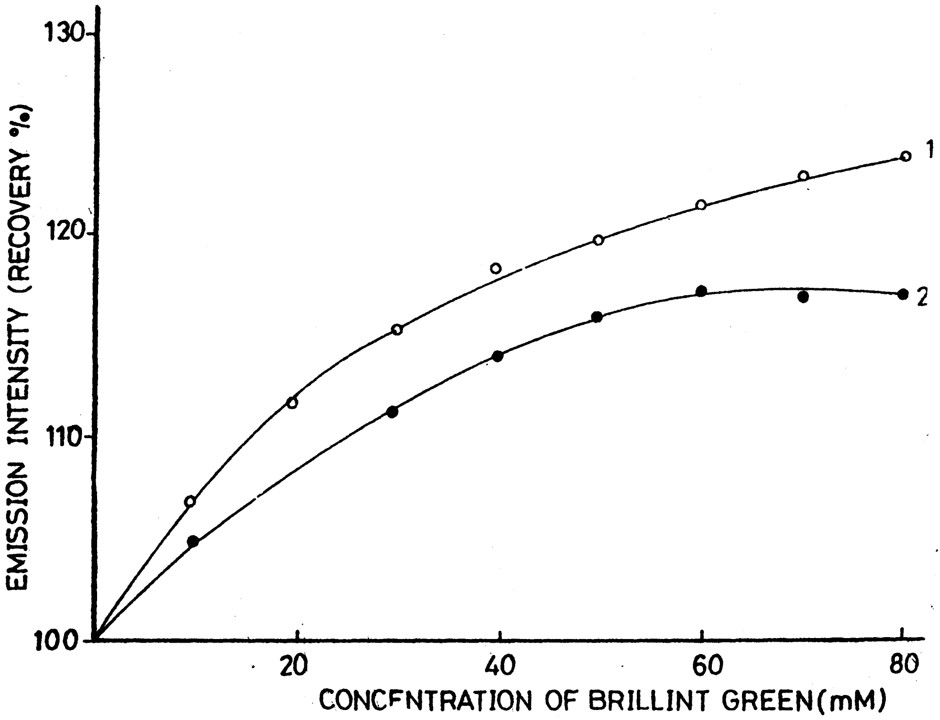

Fig. 4 Effect of brilliant green on: (1) CO emission intensity at 219 nm, (2) OH emission intensity at 281.1 nm, (Intensity of CO or OH already present in the flame is assumed to be 100; all the reading are referred to this value).

measurement above the burner top was measured. The distribution curves obtained in Figure 5(A) indicated that the distribution of Rh atoms in the flame were affected by the cations investigated. Bulewicz and Padly[16,17] suggested that, the interfering metal may be acting through a catalysis of the recombination of excess free radical concentration in the flame, thereby leading to the possibility of significant disturbance of the proportion of any analyte metal bound up in chemical form. Fig. 5(B) illustrates the behaviour of rhodium absorption in presence of interferent and after addition of 0.06 M brilliant green, the curves coincide almost exctly, this prove that rhodium absorption becomes independent on the presence of foreign cations.

Elimination of the interferences

The essential problem was to establish whether or not the addition of brilliant green can eliminate the observed interferences on rhodium absorption. The initial studies concerned the effects of different foreign ions on the absorbance values

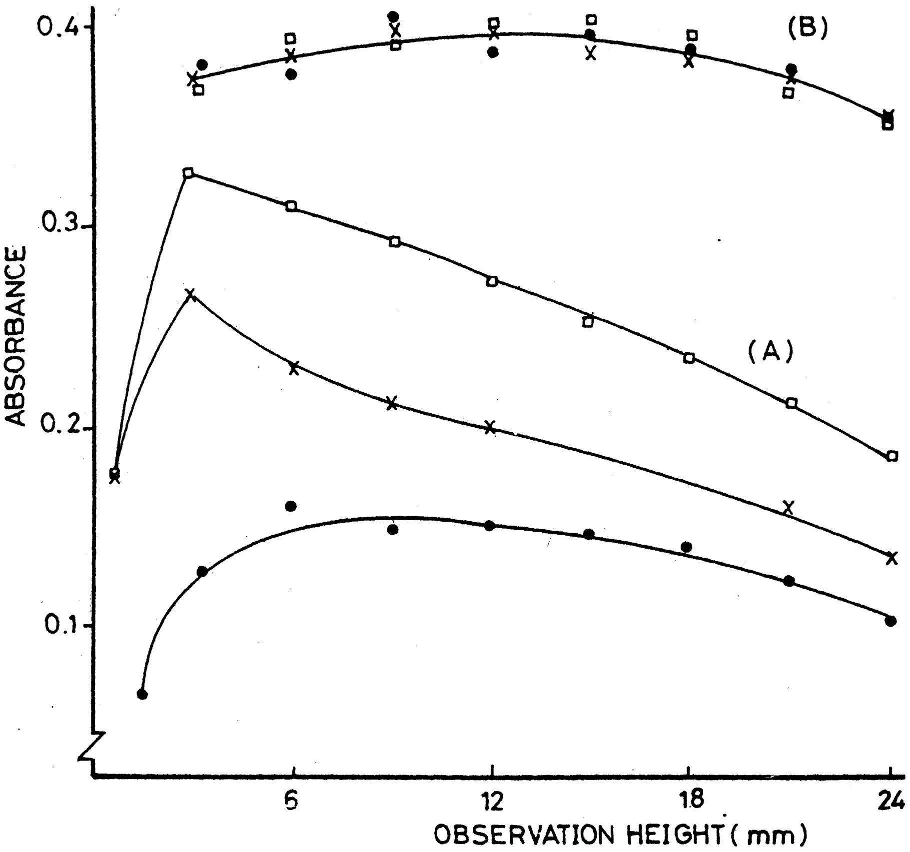

Fig. 5 Distribution of rhodium atoms as a function of observation height in presence of interfering ions(A) without brilliant green [(x), 20 ppm Rh; (●) Rh plus 200 ppm Zr; (□) Rh plus 200 ppm Zn] and (B) in presence of 0.06 M brilliant green.

of rhodium are shown in Table-1, the absorption was changed considerably by the substances studies. When brilliant green was added to samples containing interfering ions, the errors gradually disappeared (Fig.-6), and completely eliminated at point 0.6 M brilliant green. The interfering effects of several cations and anions in presence and absence of 0.06M brilliant green are summarized in Table-1. All the above data are given relative to the signal obtained for rhodium in presence of 0.06M brilliant. Under these conditions the absorbance is independent of the concentration of brilliant green over a broade range of concentration and the absorbance is nearly 1.5 times the value found in the absence of brilliant green. Typical linear calibration graphs are given in Figure-7. As shown in Table 1, the average deviation of the determinations did not exceed 1.8% after addition of brilliant green. The effect of synthetic mixtures of different cations on the

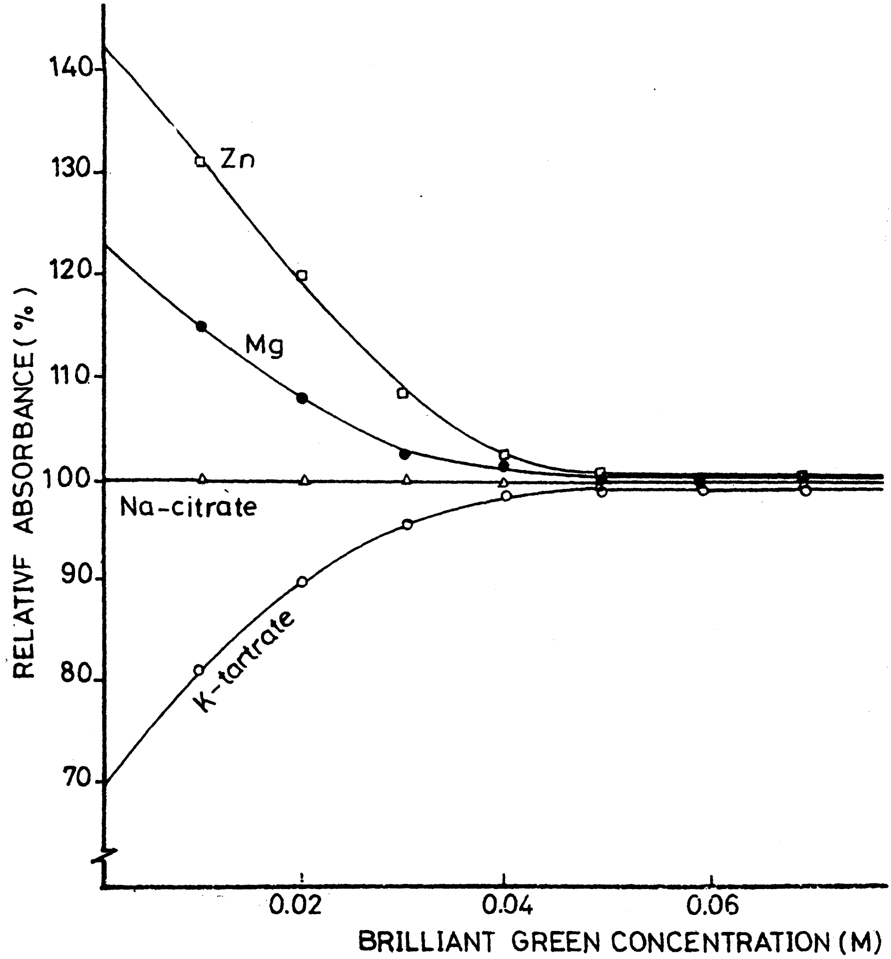

Fig. 6 Evaluation of the atomic absorption signals of rhodium (20 μg cm^{-3}) in the presence of interfering ions (200 μg cm^{-3}) as a function of brilliant green concentration.

absorption signals of Rh in presence and absence of 0.06M brilliant green is shown in Table-2.

The question arises here is, does brilliant-green reacts with interferent too? To answer this question, variable concentration of brilliant green was titrated with Rh plus interferent as zirconium or cadmium and plotted the curves. The common feature of these curves is that, the character of the absorption curves for rhodium in presence of the mentioned interferents are same as for Rh without interferent (Fig.-2). Only the calculated concentrations of brilliant green at the break points is considerably dependent on the concentration of the interferent present indicating that ligand reacts also with the interferent without affecting on atomization of the analyte in the flame.

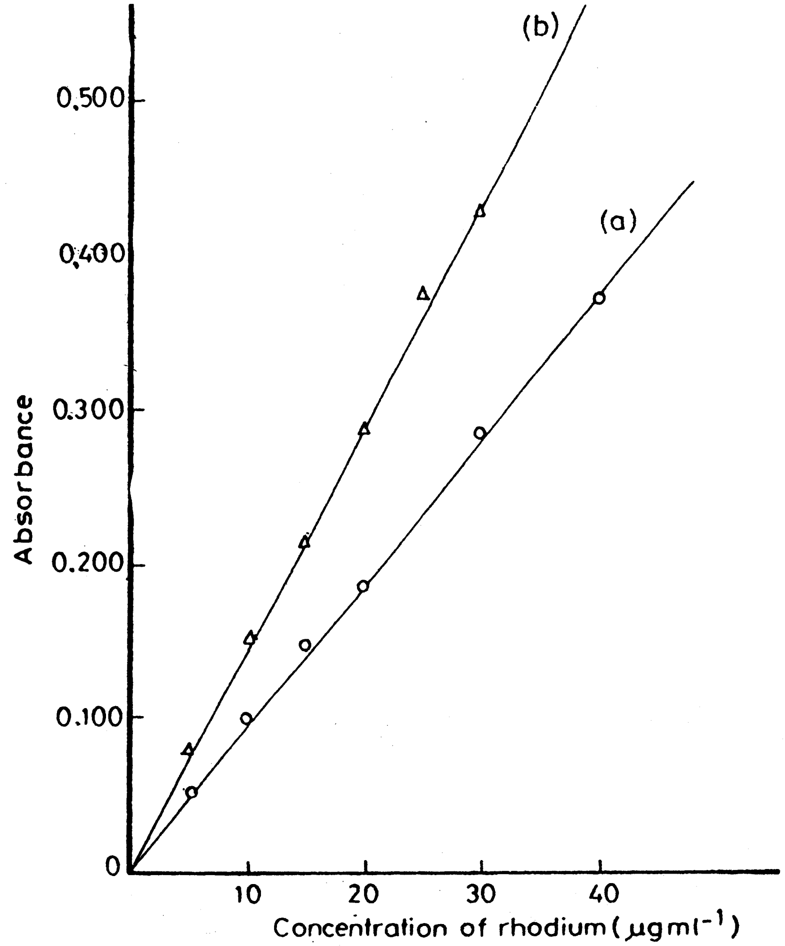

Fig. 7 Calibration graphs for rhodium: (a) obtained by simple dilution of the stock rhodium solution; (b) obtained by addition of 0.06M brilliant green.

Conclusion

The atomic absorption spectrometric determination of rhodium is not free from interferences. These interferences may be explained by the different chemical reactions that occur in the flame and the formation of compounds with different chemical stabilities. The use of brilliant-green as a releasing agent in determination of Rh serve in the production of reductive conditions favourable for atomization and forms stable complexes either with the analyte or with the interferents giving flame profile for the analyte independent of the interfering ions in the sample solution. The method offer enhanced sensitivity for Rh absorption signal by about 1.5 times its signal without use of brilliant-green.

TABLE 1
EFFECT OF DIFFERENT IONS WITH AND WITHOUT THE RELEASING AGENT (THE ANIONS WERE INTRODUCED AS SODIUM), THE CATIONS (UNLESS INDICATED OTHERWISE) AS CHLORIDES. THE CONCENTRATION OF THOSE IONS WERE 200 μg mL^{-1}; THAT DPM (SODIUM SALT OF DIPHENYLPHOSPHINOBENZENE-*m*-SULPHONIC ACID) WAS 100 μg mL^{-1}, RHODIUM CONCENTRATION, 20 μg mL^{-1}.

Added ions	Rhodium recovery (%)	
	Without	With
Ca^{2+}	146	100
Mg^{2+}	123.6	104
Sr^{2+}	114	100
Zn^{2+}	140	102
Al^{3+}	120	104
Zr^{3+}	66	100
Ru^{3+}	215	98.9
$UO_2(NO_3)_2$	118	98
$(NH_4)_2PtCl_4$	76	100
PO_4^{3-}	100	100
I^-	86	100
NH_4^+	100	100
Tartrate	70	98
Borate	89	100
Silicate	73	100
EDTA	100	100
Maleic acid	32	97
DPM	43	100

TABLE 2
MIXED EFFECT OF SEVERAL METALS WITH AND WITHOUT 0.06M BRILLIANT GREEN, THE CONCENTRATION OF EACH METAL WAS 200 μg mL^{-1} EXCEPT Pt, Ru, Zr AND Pd (100 μg mL^{-1} OF EACH) RHODIUM CONCENTRATION, 20 μg mL^{-1}.

Added substance[a]	Rh recovery (%)	
	Without	With
None	100	100
Al, Zn, Mg	134	100
Zn, Al, Ni	126	100
Ca, U, Ge	135	100
Cd, Au, Ge	125	100
In, Ge, U	140	100
Co, Zr, Ni	77	100
Ru, Si	73	98.5
Pt, Ru, Si	69	100
Ru, Pd, Pt	116	102

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