BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(10), 2611—2612 (1974)

The Determination of Ruthenium in a Sulfuric Acid Solution by Atomic Absorption Spectrophotometry

Reiko Iwata and Ikuei Ogata

National Chemical Laboratory for Industry, Honmachi, Shibuya-ku, Tokyo 151

(Received February 4, 1974)

Synopsis. The addition of sodium salts was found to make possible the determination of ruthenium in a sulfuric acid solution by atomic-absorption spectroscopy, something which is usually impossible because of the serious depressive interference of sulfuric acid.

We have recently synthesized a ruthenium complex which bears a polycyclic aromatic compound as a π-ligand and which is completely decomposable into a solution only with concentrated sulfuric acid. During the process of analyzing the ruthenium content by atomic absorption spectroscopy, we observed that sulfuric acid remarkably reduces the optical absorption of Ru. It has been reported that the atomic absorption of Ru is subject to various interferences; *e.g.*, Rowston and Ottaway[1] and Montford and Cribbs[2] have investigated the effects of various anions and cations, and Mallett *et al.*,[3] the mutual interference of noble metals. They eliminated the interferences through the addition of copper and cadmium sulphates[1] or uranium[2] as releasing agents. However, they studied only with aqueous and HCl solutions, and no reports have been made on the degree of interference encountered in a practical quantitative analysis of Ru in a sulfuric acid solution. Interference by H_2SO_4 has already been noted on other metals; it is generally eliminated by removing the sulfuric acid by vigorous fuming or by extraction with solvents. In the case of Ru, however, this technique could well cause a loss of Ru if the analysis were done by the inexperienced. The distillation of Ru as a volatile tetroxide is also recommended for the separation of Ru from complex mixtures, but it is troublesome and time-consuming, and a more direct approach would be advantageous.

After various studies, we would like to report here a very simple method in which sodium compounds are added to sample solutions.

The spectrophotometer used was a Techtron AA-100. Measurements were done with a fuel-rich air–acetylene flame[4] at a wavelength of 349.9 nm and a lamp current of 10 mA. The sample solutions used were prepared as follows: ruthenium acetylacetonate (Ru(acac)$_3$) was decomposed with concentrated acids, followed by the dilution of the resulting solutions to a Ru concentration of 50 ppm and also to stipulated values of the acid concentration. Acids of the Super-Special-Grade for precision analysis were used. The various foreign additives and acetylacetone used here were all of a reagent grade.

As may be seen in Fig. 1, which shows the interferences of H_2SO_4, HNO_3 and HCl, sulfuric acid remarkably suppressed the absorption of Ru; the absorbance was of the order of 0.01 even at a Ru concentration of 50 ppm. Therefore, the quantitative analysis of Ru in a sulfuric acid solution was practically impossible. Though not so large as H_2SO_4, nitric acid showed a fairly large suppressive effect. Further, during the process of decomposition by the boiling of Ru(acac)$_3$, $RuCl_3$, and other ruthenium-containing samples in concentrated HNO_3, a loss of Ru, presumably as a volatile oxide, was observed. Therefore, the use of HNO_3, which is generally used for atomic-absorption analysis as a less interferant acid, is undesirable in the case of Ru. Hydrochloric acid showed the least interference of the three.

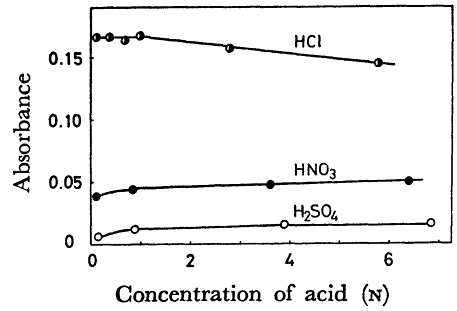

Fig. 1. Relations between interference and concentration of acids. Concentration of Ru: 50 ppm (in the cases of H_2SO_4 and HNO_3), 49 ppm (in the case of HCl).

When a large excess of acetylacetone to Ru was added to a sulfuric acid solution of Ru and the solution was allowed to stand at 50 °C, it gradually developed a pink color, indicating the formation of an acetylacetone chelate, while the absorbance increased. With the addition of 8 vol% of acetylacetone, about 5.6 times enhancement was observed in the 0.85 N H_2SO_4 solution of 48 ppm of Ru. Although the interference of H_2SO_4 can be removed in this way to a certain degree, the demerit is that this method requires a long time for the absorbance to become constant (about 10 hr).

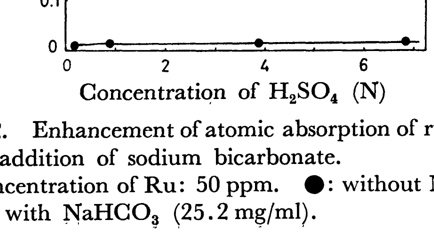

Fig. 2. Enhancement of atomic absorption of ruthenium by addition of sodium bicarbonate.
Concentration of Ru: 50 ppm. ●: without $NaHCO_3$, ○: with $NaHCO_3$ (25.2 mg/ml).

The further addition of $NaHCO_3$ to this solution containing acetylacetone in order to make the transformation of a sulfate into an acetylacetonate more efficient caused a further prominent increase of the absorbance. From the following experiments, however, it was found that this enhancement effect was not due to the formation of an acetylacetone chelate.

The addition of $NaHCO_3$ to the sample solution, even without acetylacetone, made the atomic absorption of Ru increase greatly as shown in Fig. 2. The same, but only a slight, effect of sodium salt has been reported in the case of the HCl solution of $H_2[RuCl_6]$ by Makarov and Kukushkin.[5] If the acid concentration was high, the degree of the enhancement decreased. The enhancement effect was smaller in a less interferant acid; *i.e.*, the magnitudes of the enhancement effect were in the order of $H_2SO_4 \gg HNO_3 > HCl$.

The study of the relation between the added amounts of $NaHCO_3$ and the enhancement effect revealed that the most appropriate amount of addition should be determined not on the basis of the concentration of the acid but on the basis of that of the $NaHCO_3$ in the solution. In a Ru solution of 50 ppm, it is over 4 mg/ml; especially, the range of 10–30 mg/ml is the most appropriate. When the amount of $NaHCO_3$ added was too large, the absorption tended to decrease. Further, as the amount added increases, a defective outcome develops since a separated salt attaches to the slit of the burner.

The relation between the kind of foreign additives and the enhancement effect was also studied. Table 1 shows a comparison on the basis of the relative ratio of absorbance, where the absorbance in the case of no foreign additive is defined as 1.0. Sodium compounds caused almost the same degree of enhancement, no matter what the counter anion was; this was also true in the cases of alkali and salt. Therefore, it can be seen that the enhancement is caused by Na. The effects of various sodium salts in aqueous and HCl solutions have been reported;[2] they are very complex and are not similar to those in our case of a sulfuric acid solution; some sodium compounds increased the absorbance, while some reduced it. A comparison of NaCl, $CoCl_2$, and $ZnCl_2$ showed that the higher the ionization potential of the metal, the lower the degree of relative enhancement. It is said that NH_4Cl is effective in suppressing the interference of H_2SO_4 in the determination of Mo,[6] but it caused only a very low enhancement in the case of Ru.

Table 1. Comparison of enhancement effect of foreign additives by relative ratio of absorbance[a]

Additive,[b] MX (0.3 m atom of M/ml)	Relative ratio of absorbance	Ionization potential M$^+$ (eV)
none	1.0	
$NaHCO_3$	16.1	5.138
Na_2CO_3	16.3	
Na_2SO_4	16.2	
NaOH	16.0	
NaCl	15.9	
$CoCl_2$	6.5	7.86
$ZnCl_2$	4.9	9.391
NH_4Cl	2.2	

a) Ru 50 ppm in 0.9 N H_2SO_4. b) Additives were added in a solid state.

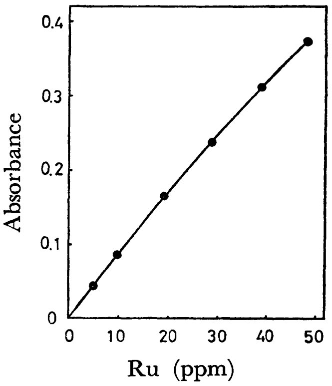

Fig. 3. Calibration curve of ruthenium in 1.48 N H_2SO_4 solution with 40 mg/ml of $NaHCO_3$ (Ru 349.9 nm, an air-acetylene flame).

Table 2. Analyses of ruthenium by atomic-absorption spectroscopy

Compound	Ru content (%)	
	Found	Calcd
$[RuCl_2(C_6H_6)Me_2SO]_2$	30.3 29.5	30.79
$[RuCl_2(C_6H_6)PBu_3]_2$	22.1 21.7	22.34

Conditions for analysis are the same as in Fig. 3.

In order to confirm the practical applicability, a calibration curve was drawn by using the method in which a certain amount of $NaHCO_3$ is added to a sample solution containing H_2SO_4. It was a straight line until the Ru concentration was approximately 20 ppm, and a slight curve in the range over 20 ppm, as is shown in Fig. 3. Using this Ru calibration curve, satisfactory results were obtained in the analyses of some known ruthenium compounds, as is shown in Table 2.

We can conclude that, this is a simple and effective enough method to remove interference in the determination of Ru in a sulfuric acid solution with a large depressive interference.

References and Note

1) W. B. Rowston and J. M. Ottaway, *Anal. Lett.*, **3**, 411 (1970).

2) B. Montford and S. C. Cribbs, *Anal. Chim. Acta*, **53**, 101 (1971).

3) R. C. Mallett, D. C. G. Pearton, E. J. Ring, and T. W. Steele, *Talanta*, **19**, 181 (1972).

4) The use of a nitrous oxide-acetylene flame was improper because it made absorbance smaller.

5) D. F. Makarov and Yu. N. Kukushkin, *Zh. Anal. Khim.*, **24**, 1191 (1969).

6) K. Yasuda and N. Hasegawa, "Atomic Absorption Analysis," Kodansha, Tokyo (1972), p. 143.