

# Periodic Research

## Semicarbazide as a New Reagent for the Detection of Silver(I)

### Abstract

Numerous organic reagents<sup>1-10</sup> form complexes with silver(I) but most of them are not selective. Only p-dimethylaminobenzylidene rhodanine<sup>5</sup> and dithiozone<sup>6</sup> have been found to be more selective for the drop analysis of silver(I). The present study, which is based on the reaction of semicarbazide with silver(I) in nitric acid medium has been used for the detection of silver(I) only on a qualitative basis. The reagent is not suitable for quantitative determination of silver because of the limited stability of the complex. The method is cold operated and instantaneous.

**Keywords:** Numerous, rhodanine<sup>5</sup>, Semicarbazide, Instantaneous, Employed, Unispeck, Spectronic, Manganous, Spectrophotometric, Sandell's, Wavelength, Deviation, Logarithmic, Ammonium Thiocyanate, Dimethyl Glyoxime, Thiourea.

### Introduction

In our earlier work mention has been made of the formation of Copper (II) complex with Semicarbazide, our present work deals with the based on the reaction of Semicarbazide with silver(I) in nitric acid medium has been used for the detection of silver(I) only on a qualitative basis.

### Aim of the Study

The aim of the investigation is to describe the reaction of Semicarbazide as a new reagent for the detection of silver(I). This method is cold operated and instantaneous.

### Experimental

#### Materials

Silver nitrate and semicarbazide (both B.D.H) and other reagent of either B.D.H. or E. Merck grade were used. The cations were used as nitrates or carbonates while the anions were used as sodium or potassium salts. A micrometer syringe was used for measuring the drop volume while graduated droppers were employed for adding the solutions of the interfering ions. Silver nitrate stock solution ( $2\mu\text{g/ml}$ ) and semicarbazide solution (0.1% W/v) were prepared in double distilled water. The solutions of interfering ions were either in double distilled water or in 0.01 N nitric acid. Hilger-Unispeck-Spectronic 20 was used for measuring absorbance.

#### Procedure

1. Spot test: A drop of silver(I) solution ( $2\mu\text{g/ml}$ ) was taken on a black spot plate and one drop of 0.01 N nitric acid was added followed by a drop of 0.1% aqueous solution of the reagent. A white precipitate formed instantaneously, which gradually turned to grey violet. This indicated the presence of silver(I). In another similar test, a drop of 2% manganous nitrate solution followed by a drop of 2.5 N sodium hydroxide solution was added soon after the formation of the white precipitate. A black stain was obtained. Sensitivity:  $2\mu\text{g/ml}$ , concentration limit: 4: 100000.
2. Spectrophotometric method: A 5 ml of aliquot, containing 0.6  $\mu\text{g/ml}$  of silver was taken in a 25 ml measuring flask to which 2 ml of 0.01 N nitric acid and 15 ml of 0.1% aqueous reagent were added. The volume was made up to the mark with double distilled water. The absorbance was measured within 40 min at 520 nm against reagent blank.



**Dazy Kumari**

Lecturer,  
Dept. of Chemistry,  
Urdu College,  
Gopalganj, Bihar, India

## Discussion

The system silver-semicarbazide absorbs maximum at 520 nm and the reagent has nil absorption at this wavelength. The molar absorptivity,  $\epsilon$  is found to be  $8.6 \times 10^3 \text{ lit. mole}^{-1} \text{ cm}^{-1}$  the range of pH value for no change in absorption has been found to be 1-7. So a p of 4 was selected. Four fold excess of reagent over silver is required for full colour development, but further excess does not affect absorbance. Beer's law is obeyed upto  $6 \mu\text{g/ml}$  of silver. Sandell's sensitivity of reaction comes to  $0.0056 \mu\text{g/cm}^2$ . For 6 aliquots of standard solution ( $6 \mu\text{g/m}$  of silver), the standard deviation and relative deviation have been found to be  $\pm 3.1 \times 10^{-3}$  and  $\pm 0.94\%$  respectively.  $\lambda_{\text{max}}$  showed that only one compound existed, at least up to 40 min. Job's and Logarithmic methods show the metal to ligand ratio to be 1 : 1.

## Interferences

The effect of divers ions for determination of  $4 \mu\text{g/ml}$  of silver(I) was studied at 0.01 N nitric acid concentration of the aqueous phase. Varying amounts of the foreign ions were taken with a fixed amount of silver and the colour was developed and measured as described above.

The tolerance of other ions (concentration in  $\mu\text{g/ml}$ ) is found to be as follows :  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$ , (1000);  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$  (50),  $\text{Hg}^{2+}$  ( $10^3$ );  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{3+}$ ,  $\text{Fe}^{2+}$ , (10),  $\text{Pd}^{2+}$ , (8) and  $\text{PO}_4^{3-}$ , (30) can be tolerated. However,  $\text{Pd}^{2+}$   $\text{Cl}^-$ ,  $1^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{Co}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{PO}_4^{3-}$  are destroyed by dilute nitric acid.  $\text{Hg}^{2+}$  can be masked with 5% KCN Solution.  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  can be masked with EDTA and thiourea respectively,  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$  by dilute nitric acid.  $\text{Co}^{2+}$  is masked with ammonium thiocyanate solution.  $\text{Pd}^{2+}$  has a little chance of being associated with silver(I) salt. If it is present, it can be removed by dimethyl glyoxime.  $\text{SO}_4^{2-}$  interferes only when it is 25% of the amount of silver ion is solution.

## Conclusion

Detection of silver in silver coin: A Silver coin of approximately know composition (Ag, 50% ; Cu, 35-38% ; Al, Zn and Sn, 15-12%) was dissolved in 2N nitric acid. 5 ml of the solution were taken in a 100 measuring flask and diluted with water to the mark. 25 ml of the dilute solution were treated with thiourea to precipitate copper. After filtration, 5 ml of the filtrate were taken in a 25 ml measuring flask. Four fold excess of the reagent was added and diluted to the mark. The absorbance was measured as above. Silver was also detected by spot test technique described earlier.

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