

SHORT COMMUNICATION

Determination of Copper, Total Chromium and Silver in Impregnated Carbon

Beer Singh, S. Madhusudanan, C.G. Padma Kumar,
S.R.S. Sachan, S.K.Pandey and Seema Agarwal

Defence Research & Development Establishment, Gwalior - 474 002

ABSTRACT

Carbon samples were impregnated with ammonical solutions of silver salt alone and in combination with *Cu* and *Cr* salts. The impregnated samples were characterised for *Cu*, total *Cr* and *Ag*. Copper was extracted as $CuCl_2$ using concentrated *HCl* and *Cr* with *NaOH*. Silver was extracted from impregnated carbon using HNO_3 and sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) and ashed impregnated carbons using aqua regia. The extracted metals in their solutions were quantitatively determined by titrimetric method and atomic absorption spectroscopy. The results were within acceptable limits of error. Sodium thiosulphate is recommended for extraction of *Ag*, as it accomplishes complete leaching of *Ag* faster than the other extracting agents.

1. INTRODUCTION

Activated carbons impregnated with *Cu* (II), *Cr* (VI) and *Ag* (I) salts are used for the removal of low molecular weight gases from air streams¹⁻³. The impregnants present are in the range 6.0–8.0 per cent *Cu* (II), 2.5–3.5 per cent *Cr* (VI) and 0.05–0.2 per cent *Ag* (I). On ageing⁴⁻⁷ in hot and humid atmosphere, they lose the protection capacity against cyanogen chloride, hydrogen cyanide, phosgene, etc. due to reduction of *Cu* (II) and *Cr* (VI) to their lower oxidation states. Therefore, the impregnant evaluation in carbons is of utmost importance in the selection of a suitable adsorbent for NBC protection systems.

Copper and Chromium in their different oxidation states were estimated by extracting them in acidic and alkaline media, respectively in earlier

procedures⁴. Katz and Salem⁸ described a method for the determination of hexavalent *Cr*. However, Hammerstorm,⁴ *et al.* have not provided any specific method for the extraction of *Cu* and *Cr*. Extraction with HNO_3 for *Ag* estimation from impregnated carbons did not yield quantitative results. The chloride ions present in the native carbon seemed to interfere leaching of *Ag* with acid due to formation of insoluble $AgCl$. Also, no extraction procedure for *Ag* in trace quantities is available in literature. This investigation describes a suitable extraction procedure for the estimation of *Cu*, total *Cr* and *Ag* in impregnated carbons.

2. EXPERIMENTAL PROCEDURE

Activated carbon prepared from coconut shell, as received from the Active Carbon (I) Ltd., Hyderabad, was screened to 12 x 30 BSS mesh size

and impregnated with ammonical solutions of *Cu* (II), *Cr* (VI) and *Ag* (I) salts in various proportions. The dried samples were evaluated for *Cu*, total *Cr* and *Ag*. The methods used for analysis of these impregnants are:

2.1 Estimation of Copper

Impregnated carbon (10 g) was digested with concentrated *HCl* (50 ml) and heated for 30 min to reduce the volume of the solution to 10 ml. Distilled water (50 ml) was added to this, and heated to boiling and filtered hot through Whatman filter paper (No. 42). This operation was repeated six times to ensure complete extraction. The filtrate was made up to a known volume and *Cu* estimated using titrimetric method⁹ and atomic absorption spectroscopy (AAS) technique. The results are given in Table 1.

2.2 Estimation of Total Chromium

Impregnated carbon (10 g) was digested with *NaOH* (25 g) and 50 ml distilled water. This was heated slowly for 25 min, diluted with 50 ml distilled water and boiled for 5 min. The solution

Table 1. Analysis of impregnated carbon for its copper contents

Sample	Copper (%)		
	Theoretical	Calculated	
		Iodometric	AAS
A	5.70	5.50	
B	5.70	5.50	
C	5.70	5.69	—
D	5.70	5.83, 5.73	5.51
E	5.70	5.56	—
SN1	6.05	6.15	5.95
SN2	6.05	5.91	5.97
SN8	6.14	5.80	5.58
	6.55	6.30	6.40
II	6.55	6.32	6.40
III	6.72	6.46	
IV	6.51	6.66	—
	7.00	6.47	6.67
2	7.00	7.03	6.77
3	7.00	6.67	
4	7.00	6.99	

was then filtered through Whatman filter paper (No.42). The filtrate contains the total *Cr* as Na_2CrO_4 . This operation was repeated six times. The filtrate was neutralised with 42 ml concentrated *HCl* and made up to a known volume for the estimation of total *Cr* by titrimetric¹⁰ and AAS techniques. Results are given in Table 2.

Table 2. Analysis of impregnated carbon for total chromium contents

Sample	Chromium (%)		
	Theoretical	Calculated	
		Iodometric	AAS
A	2.35	2.00	
B	2.35	2.05	
C	2.35	2.31	
D	2.35	2.31	
E	2.35	2.30	
I	2.80	2.70	
II	2.80	2.62	3.05
III	2.88	2.76	3.00
IV	2.78	2.60	
	3.00	3.10	
2	3.00	3.03	
3	3.00	3.04	3.14
4	3.00	3.05	3.07
5	3.00	3.05	3.13

2.3 Estimation of Silver

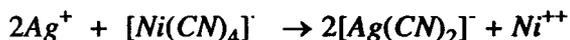
2.3.1 Extraction with Nitric Acid

Impregnated carbon (10 g) was heated with concentrated *HNO*₃ (25 ml) till approx 5 ml remained in the evaporator. Nitric acid (25 ml) was added again and heated till the volume was reduced to 1.0–2.0 ml. Distilled water (50 ml) was added and heated to boil for 5 min and the hot solution filtered through Whatman filter paper (No. 42). The operation was repeated six times. The filtrate was made up to a known volume for *Ag* estimation using AAS. Results are given in Table 3.

2.3.2 Extraction from Ashed Sample

Impregnated carbon (10 g) was heated in a silica crucible placed in a muffle furnace at 650 °C for 6 hr. The ashed carbon was digested with 50 ml aqua regia and heated till the volume was

reduced to 5 ml, then 50 ml distilled water was added and heated for 10 min. The solution was filtered hot through Whatman filter paper (No.42). The process was repeated four times with 25 ml distilled water. The residue containing *AgCl* along with filter paper was digested overnight in 100 ml liquor ammonia. The solution containing $[Ag(NH_3)_2]Cl$ was filtered, 25 ml distilled water containing 5 ml ammonia added to the residue, stirred gently for 2 min and again filtered. The operation was repeated four times. The filtrate along with washing was heated till the volume was reduced approx to 10 ml. Silver chloride thus formed was estimated using potassium nickel cyanide. The latter liberated Ni^{++} which were titrated¹¹ against ethylene diaminetetra acetic acid (EDTA). The results are summarised in Table 4. The generation of Ni^{++} follows the chemical equation:



2.3.3 Extraction with Sodium Thiosulphate

Impregnated carbon (10 g) was digested with $Na_2S_2O_3 \cdot 5H_2O$ (10 g) in 50 ml distilled water and heated gently for 30 min. After further adding 50 ml distilled water, the solution was heated to boil and filtered hot through Whatman filter paper (No. 42). The operation was repeated six times for complete extraction of *Ag* as $Ag_2S_2O_3$. In the final step, 50 ml of hypo solution (5 per cent) was used for the extraction of residual *Ag*, if any. The filtrate was made up to a known volume for *Ag* estimation by AAS. The results are presented in Table 4. Calibration curves were made for every AAS determination of total *Cr*, *Cu* and *Ag*.

Table 3. Analysis of impregnated carbon for silver contents using nitric acid as extract

Sample	Silver (%)	
	Theoretical	Calculated
A		0.04
B		0.02
C		0.06
D		0.10

3. RESULTS & DISCUSSION

The data (Tables 1,2,3 and 4) of *Cu*, total *Cr* and *Ag* estimation indicated that the methods for quantitative determination of these metals in impregnated carbon are reproducible and reliable except that of *Ag* by HNO_3 extraction. This may be due to the interference of chloride ions and negligible solubility of *AgCl* in HNO_3 .

Copper was extracted with concentrated *HCl* and estimated iodometrically against hypo and also using AAS. No interference was observed due to *Cr* and *Ag* with active *Cr* (VI) passing into inactive *Cr* (III) and *Ag* into *AgCl*. Chromium (III) remained in solution with *Cu* (II) and did not pose any problem, as it was unreactive to hypo. Silver chloride was retained by carbon.

The results (Table 1) showed that both titrimetry and AAS methods are comparable indicating the absence of *Cr* (VI) in the solution extracted for *Cu* and therefore either of the methods can be used to determine *Cu* in the extract. The

Table 4. Analysis of impregnated carbon for silver contents

Sample	Silver (%)		
	Theoretical	Calculated	
		(a) *	(b) **
SN1	0.20	0.19, 0.20	0.21
SN2	0.40	0.41, 0.40	0.38
SN3	0.10	-	0.11
SN4	Nil	Nil	Nil
SN5	0.06	-	0.06
SN6	0.26	0.25, 0.26, 0.27	0.25
SN7	0.61		0.60
SN8	0.88		0.90
SN10	0.48		0.52
SN11	0.82	-	0.74
A	2.00	2.03	
	0.19	0.20, 0.21	0.20
II	0.19	0.16, 0.17	0.20

Ashed the samples and *Ag* was estimated in *AgCl* using $K_2[Ni(CN)_4]$ against EDTA.

** Extracted *Ag* in the sample using $Na_2S_2O_3$ and estimated using AAS technique.

AAS when used to find the presence of *Cr* in the solution extracted for *Cu* showed it in the range 0.70–0.90 per cent. This can be ascribed to *Cr* in the oxidation states other than *Cr* (VI) as it reduces to its lower oxidation¹² states when boiled with *HCl*. The results on total *Cr* (Table 2) indicate that both the techniques, iodometric and AAS, are comparable and therefore any one can be used. The advantage of AAS technique was that it showed the presence of *Cu* (II) in concentration as low as 0.1–0.3 per cent in the extracted total *Cr* solution, possibly due to slight solubility of *Cu(OH)₂* produced due to reaction of *Cu* salts present over impregnated carbon with *NaOH*.

It is important to know the ratio of *Cr* (VI) to *Cr* (III) to predict the protection/breakthrough time offered by Whetlerite against cyanogen chloride. Ross¹³, *et al.* determined the ration of *Cr* (VI) to *Cr* (III) using peak area obtained from X-ray photoelectron spectroscopy. This method does not provide the absolute value for *Cr* (III), and hence there is a need to address this aspect.

Estimation of *Ag* in trace quantities in impregnated carbons poses great difficulties, seemingly, due to the presence of chloride ions in the raw activated carbon used for impregnation. Various methods were tried to extract *Ag* using *HNO₃*, ammonia after converting *Ag* to *AgCl* in ashed sample and *Na₂S₂O₃.5H₂O*. Use of *HNO₃* did not result in complete extraction of *Ag* and gave nonconcordant results. It appears that the chloride ions react with *Ag⁺* to yield insoluble *AgCl*, which is only sparingly soluble in concentrated *HNO₃*.

The estimation of *Ag* from impregnated carbon after ashing is a time-consuming process. However, the extraction of *Ag* with *Na₂S₂O₃.5H₂O* and its estimation using AAS is sensitive, accurate and rapid. The data indicate that these two methods are highly comparable, but the latter method being rapid and simple, is recommended for the estimation of trace quantities of *Ag* in impregnated carbons.

4. CONCLUSION

Impregnated carbon is an essential component of NBC protection/filtration systems, and therefore its analysis for the constituents needs accurate and

simple methods. The methods developed for the determination of *Cu*, total *Cr* and *Ag* are reproducible and also meet the stringent requirements of accuracy and reliability. The AAS provides more accurate results generally, and hence is recommended for the estimation of these metals in impregnated carbon.

ACKNOWLEDGEMENTS

The authors are thankful to Shri R.Vaidyanath Swamy, Director, DRDE, Gwalior, for suggesting the methods for estimation of *Ag*, Shri Rabinder Nath for helping in establishing procedures for the determination of metals. Sarvashri M.V.S. Suryanarayana and N.B.S.N. Rao for suggestions during this study.

REFERENCES

- Noyes, W.A. (Jr). Military problems with aerosols and non-persistent gases. Division 10 NDRC Summary Technical Report, Vol. 1 (1946).
- Barnir, Z. & Aharoni, C. Adsorption of cyanogen chloride on impregnated active carbon. *Carbon*, 1975, **13**, 363.
- Aharoni, C. & Barnir, Z. Efficiency of adsorbents for the removal of cyanogen chloride. *Am. Ind. Hyg. Assoc. J.*, 1978, **39**, 334.
- Hammarstrom, J.L. & Sacco, A. (Jr). Investigation of deactivation mechanisms of ASC Whetlerite charcoal. *Journal of Catalysis*, 1988, **112**, 267.
- Bac, N.; Hammarstrom, J.L. & Sacco, A. (Jr). Thermal decomposition studies on copper-chromium-silver impregnated activated charcoal. *Carbon*, 1987, **25** (4), 545.
- Ehrburger, P.; Henlin, J.M. & Lahaye, J. Ageing of cupric oxide supported on activated charcoal. *Journal of Catalysis*, 1986, **100**, 429.
- Ehrburger, P.; Dentzer, J.; Lahaye, J.; Dziejzini P.; Fangat, R.; Thermal behaviour of chromium trioxide deposited on carbon. *Carbon*, 1990, **28** (1), 113.

8. Katz, S.A. & Salem, H. Comparison of spectrophotometric methods for the determination of hexavalent chromium in Whetlerite. *Spectroscopy*, 1986, 1, 35.
9. Vogel, A.I. A text book of quantitative inorganic analysis, Ed. 3. The English Language Book Society and Longmans, 1961. 358 p.
10. Vogel, A.I. A text book of quantitative inorganic analysis, Ed. 3. The English Language Book Society and Longmans, 1961. 350 p.
11. Vogel, A.I. A text book of quantitative inorganic analysis, Ed. 3. The English Language Book Society and Longmans, 1961. 450 p.
12. Mellor, J.W. A comprehensive treatise on inorganic and theoretical chemistry, Vol. XI. Longmans Green & Co, New York, 1954. 231 p.
13. Ross, M. M.; Colton, R.J. & Deitz, V.R., The study of Whetlerite surfaces by X-ray photoelectron spectroscopy. *Carbon*, 1989, 27, 492.

Contributors



Dr Beer Singh joined DRDO at the Defence Research & Development Establishment (DRDE), Gwalior. He has been working on defence against chemical warfare agents. He has developed the impregnation process for active carbon and silica gel for protection and detection of chemical warfare agents, respectively. He also developed evaluation methods for the protective equipment.



Mr S Madhusudanan joined DRDO at DRDE, Gwalior. He has been working on the evaluation of nuclear, biological and chemical (NBC) individual protective equipment. He has also worked for the development of impregnation process for active carbon for use in NBC filtration systems.



Mr SRS Sachan joined DRDO at DRDE, Gwalior. He has been working on the detection of toxic impurities in water. He has also developed water poison detection kit.

Mr SK Pandey obtained his MSc (Physics) in 1997. He joined DRDO at DRDE, Gwalior, in 1991. Presently, he is working as Technical Assistant at the Defence Standardisation Cell, Delhi.