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ANALYSIS OF TEDA ON ASC-WHETLERITE CHARCOAL (U)

by

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ABSTRACT

A new procedure for the analysis of the TEDA content on ASC whetlerized charcoal has been developed. The results of the analysis of commercially-supplied and custom-made ASC whetlerites co-impregnated with TEDA are presented. Some background information on this analytical procedure is also presented.

RÉSUMÉ

Une nouvelle procédure d'analyse de la quantité de TEDA dans le charbon activé ASC-whetlerite a été développée. Les résultats de l'analyse d'échantillons de sources commerciales et de charbons activés ASC-whetlerite co-imprégné de TEDA préparés en laboratoire sont présentés. Une revue des antécédents de cette procédure analytique est aussi présentée.

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1.0 INTRODUCTION

In the course of research and development on charcoal, chemical impregnants were incorporated onto charcoal surfaces to afford better protection against some CW agents. The use of copper, chromium, and silver as charcoal impregnants (the 'ASC' in ASC-whetlerite) originated in 1942 (1) and is still regarded as the best available multi-purpose adsorbent for military air filters. However, recent studies on the health hazards of tri- and hexavalent chromium (2) have demonstrated that they are both cancer-inducing agents. Although the absorption of chromium (VI) by the lungs after inhaling charcoal dust from testing a military canister containing ASC-whetlerite is not sufficient to cause any harm (2), it is desirable that the percentage of chromium (VI) in ASC-whetlerite be reduced, if not completely removed.

Recently, triethylenediamine (TEDA), more formally known as DABCO or (1, 4-diazabicyclo [2,2,2] octane), has received the attention of British, American and Canadian investigators as a supplementary additive for enhanced CK-protection. One implication of this is that it may be possible to partially or totally substitute the chromium with TEDA. TEDA appears to be more useful than other amines (e.g. pyridine or hexamethylene tetramine) used earlier as adsorption enhancing agents on charcoals (1). The major advantage lies in the fact that TEDA does not desorb from the charcoal surface to any appreciable extent. A recent report (3) from Westvaco Inc. indicates that the application of 1.5% TEDA to a laboratory ASC-whetlerite provides a significant increase in CK life for both fresh and aged charcoal. However, the same charcoal without any chromium has a lower CK life, even when the TEDA content is increased to 7.5%. This indicates that it may not be possible to completely replace chromium with TEDA in order to provide adequate protection against CK.

In support of this increased interest in TEDA impregnated charcoal it has become apparent that there is a need for an accurate analytical method which allows accurate TEDA determinations. This technical note describes a method which achieves this goal. CANADA

1.1 BACKGROUND

Air filters containing activated charcoal impregnated with TEDA have been widely used in the nuclear reactor industry for the monitoring

and trapping of radioactive iodine and methyl iodides (4). The trapping mechanism is based on the stable 1:1 complex formed between the amines and the radioactive iodine. Of the known $\widehat{n-\sigma}$ types of charge-transfer complexes, those involving iodine and amines as acceptor and donors respectively have been most extensively studied (5). In these complexes, the intermolecular bond is localized, and the N-I-I moiety is linear (6). For monofunctional amines, such as ammonia, the complexes are strong with formation constants in the range of 10^{2} - 10^{4} l/mole at 20°C and enthalpies of formation between -5 and -12 kcal/mole. Complexation involving multi-functional donors and acceptors (such as TEDA and iodine) pose difficulties in determining the nature and extent of interactions between active sites and an understanding of how complexation at one site influences the activity of the uncomplexed site.

TEDA is a cage-like ditertiary amine. It is characterized by high symmetry, globular structure, high melting point (158°C), and contains two exposed nitrogen atoms whose unshared electron pairs are free of steric hindrance. The preparation procedure for the TEDA:I_2 complex has been well documented (6,7). The same 2:1 complex of iodine to TEDA forms when the concentration of iodine equals or doubles the concentration of TEDA (6). This is contrary to the complex formed between bromine and the diamine, in which the mono-adduct between bromine and TEDA is also formed (5c, 8).

The detailed theoretical considerations of this diamine-halogen charge-transfer complex is very complicated and beyond the scope of this report. However, this TEDA-iodine complex forms the basis on which the concentration of TEDA on charcoal is determined. TEDA is strongly adsorbed onto the charcoal surface, therefore after it is leached out from the charcoal surface with acid, it has to be complexed immediately. The stable TEDA-iodine complex is an obvious choice. The TEDA-iodine complex is a high-melting solid which is insoluble in most organic solvents and decomposes in the presence of acids. Therefore allowances have to be made so that the TEDA concentration can be determined gravimetrically.

Due to the above consideration, it becomes necessary to introduce carbon standards so that the results from unknown samples may be compared. Since the loading level of TEDA on charcoal may typically vary from 0 to 10%, at least two standards, containing about 2 and 6% of TEDA, have to be employed to cover this range. Each standard is also duplicated to take care of experimental variation. Note that this procedure involving the reference standards is the most critical step in the whole analysis. The gravimetric factor obtained for the reference standards will determine:

(i) The extent of interference from the metal ions on the ASC-charcoal; (these ions may be leached out by the acid and complex with the free TEDA);

(ii) the extent of complexation between TEDA and iodine in the acid medium; and

(iii) the extent of the solubility of the final TEDA-I_2 complex.

All three factors are subject to variability due to technique, reagent purity, and consistency of the carbon samples.

2.0 REAGENTS AND EXPERIMENTAL

The TEDA was obtained from Aldrich Chemical Co. It was purified by sublimation under vacuum at 35°C until a constant melting point was obtained. The purity was checked by ^1H and ^{13}C nmr spectroscopy, and the melting point was found to be 157-158°C. After sublimation, the white TEDA crystals were sealed by flame in glass ampules, in amounts either of 0.15 or 0.65 grams. The iodine employed was from Fisher Scientific Co. and was also purified by sublimation. The potassium iodide was also obtained from Fisher Scientific Co. The 0.1 N iodine solution was prepared from a standard procedure (9). This reagent was always prepared fresh for each experiment. The sulfuric acid used was diluted from concentrated sulfuric acid supplied by J.T. Baker Chemical Co.

The charcoals used in these experiments were all obtained from Calgon Carbon Co. The standard charcoal used is from batch-1048, which is a standard ASC-whetlerite containing copper, silver and chromium. The TEDA-loaded charcoals were research samples of ASC-charcoal loaded with specified amounts of TEDA. Two custom-made TEDA-loaded charcoals were also tested.

All charcoal samples were dried in an oven at 105°C overnight before the analysis.

2.1 DETERMINATION OF TEDA CONTENT IN CHARCOAL SAMPLES

Weigh 10 grams of the granular carbon to be analyzed to ±0.001 grams. Weigh four 10-gram samples of a standard ASC carbon that have not been impregnated with TEDA to ±0.001 grams into four 30 ml weighing bottles fitted with ground glass caps. Add about 0.15 grams (accurately weighed to ±0.001 grams) of TEDA to each of two standard ASC carbon samples, and about 0.65 grams (accurately weighed to ±0.001 grams) of TEDA

to the two remaining ones. Allow the mixture to equilibrate for 2½ hours to permit adsorption of TEDA by the carbon. Occasional shaking of the weighing bottles helps the adsorption of TEDA. Transfer each of the samples (including any leftover TEDA crystals) to separate 400 ml beakers and add 100 ml of 1N H_2SO_4 to each. Cover with a watch glass and place each beaker on a hot plate. Bring to a boil and boil for 15 ± 1 minute. Remove from hot plate and allow to cool to room temperature. Filter through a Millipore filter (3.0 µm) apparatus into a 250 ml filter flask under reduced pressure. Wash beaker, watch glass, and carbon with 3x 25 ml portion of deionized water. Quantitatively transfer filtrate to a 400 ml beaker and wash filtering flasks with 2x 10 ml portion of deionized water. Add, with stirring, 200 ml of 0.1 N iodine solution, and cover the beaker with a watch glass. The supernatant solution on top of the greyish to reddish precipitate should have a dark reddish brown color indicating an excess of iodine. If a greenish tint persists, add more iodine solution until the supernatant is reddish brown. Allow the mixture to stand for ½ to 1 hour. Quantitatively filter each solution through a separate dried, weighed, 50 ml medium porosity filter crucible under reduced pressure. Wash each beaker with 2x 25 ml of deionized water, being careful to transfer all the precipitates into the crucible. Wash the precipitate with 2x 25 ml of deionized water. Place the crucible into a 150 ml beaker, cover with a watch glass, and dry the precipitate overnight in a 105°C oven. Reweigh crucible after cooling in a desiccator and determine the weight of precipitate by the difference from original weight of empty crucible. Determine the gravimetric factor as follows:

$$A = \frac{B}{C}$$

where A = gravimetric factor,
B = weight of precipitate from the standard ASC carbon sample,
C = weight of TEDA used.

The final gravimetric factor D, is then the arithmetic mean of the four determinations. These four values should not deviate by more than 5%, otherwise the procedure for the reference standards has to be repeated. Calculate the percent TEDA on the unknown carbon samples as follows:

$$\% \text{ TEDA} = \frac{E \times 100}{D \times F}$$

where D = final gravimetric factor from above,
E = weight of the precipitate,
F = weight of the carbon sample used.

3.0 RESULTS AND DISCUSSION

The gravimetric factor determined for the four charcoal standards was 4.52 with a standard deviation of less than 5%. This value for the gravimetric factor is different from the value of 2.3 obtained by the Calgon (10) procedure from which the previous DND specification (11) was derived. It is believed that the reason for the observed difference in gravimetric factors results from ignoring the solubility of the TEDA.I_2 complex in water in the previous DND specification; subsequent to this study the specification was modified.

The experimental results of the TEDA analysis on unknown charcoal samples are listed in Table 1. There was no information, such as preparation procedure, purity level, and accuracy of the TEDA concentration supplied with the TEDA-loaded ASC-charcoals from Calgon Carbon Co. The analysis results show consistently lower values compared to the manufacturer-specified values, although the analysis values are in the same order of magnitude as the "true" values. This consistent lower value of TEDA content may also be due to loss of TEDA (by sublimation or oxidation in air) during the drying of charcoal. A quantitative estimate of this loss of TEDA cannot be easily determined.

TABLE 1: TEDA Analysis

ASC/TEDA Sample	Inorganic Impregnants	% TEDA	% TEDA from analysis	Difference
Calgon-1[a]	Cu, Cr (VI), Ag	10%[c]	9.21%	0.8
Calgon-2[a]	Cu, Cr (VI), Ag	6%[c]	5.45%	0.5
Calgon-3[a]	Cu, Cr (VI), Ag	3%[c]	2.41%	0.6
Calgon-4[a]	Cu, Cr (VI), Ag	1.5%[c]	1.20%	0.3
DREO-1[b]	Cu, Cr (VI)	6.47%[d]	6.19%	0.3
DREO-2[b]	Cu, Cr (VI)	0.27%[d]	0.22%	0.1

[a] Research samples supplied from Calgon Carbon Co.

[b] TEDA-loaded ASC-charcoal prepared from BPL charcoal at DREO.

[c] This value for TEDA-loading level was supplied by the manufacturer (no indication of accuracy of this data was provided).

[d] Estimated from the % TEDA in the spraying solution, and the volume of the spraying solution used.

Since there is a variation of about 5% in the gravimetric factor, one would expect that the analysis result for TEDA would vary by at least that much. If one further assumes that the experiments erred on the low side, and adjustments of the experimental data are made accordingly, then there is a better agreement between the analysis results and the "true" value.

Some may argue that this experimental procedure is too time-consuming, especially in the drying of the TEDA-iodine complex. An alternate method would be to do an iodometric titration (with a thiosulfate solution) to determine the iodine concentration in the solution after complexation has occured and the TEDA-I_2 complex removed. This will yield the concentration of TEDA-iodine complex indirectly. This alternate method was not attempted in this laboratory because higher precision, such as exact concentration of the 0.1 N I_2 solution, titration volumes etc., is required. Also, the I^- used in the 0.1 N I_2 solution may be oxidized by the Cr(VI) and Cu ions leached out from the charcoal. This extra effort is more than compensated by the more time-consuming gravimetric method.

Another feature of this gravimetric procedure is that knowledge of the exact chemistry of the TEDA-iodine complex is not required. A gravimetric factor could be obtained from the charcoal standards to account for all of the experimental variations discussed in Section 1.1.

4.0 CONCLUSIONS

A procedure was developed for the analysis of TEDA concentration on ASC-charcoal loaded with TEDA. The results are satisfactory for a TEDA-loading level from 0.2 to 10%.

5.0 RECOMMENDATIONS

It is recommended that the analytical procedure for the analysis of TEDA described in this report be adopted in DND Specification D-77-001-013/SF-001 for TEDA/ASC carbon.

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