

Via Memorandum Report 103

SPECTROSCOPIC STUDIES OF NUCLEAR SUBMARINE ATMOSPHERES

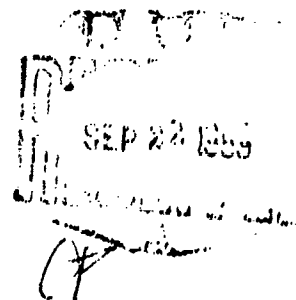
I. Desorption and Analysis of Contaminants from Hopedite

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ABSTRACT

A semi-micro analytical method is described for desorbing contaminants from Hopenlite, an oxide catalyst used in the purification of submarine atmospheres. The method was especially developed for recovering contaminants adsorbed on catalyst samples rendered explosive by incorrect usage.

The contaminants are desorbed from the Hopenlite by passing pressurized steam through a column of the catalyst. The various compounds are eluted from the column successively in a manner analogous to a liquid chromatogram. The desorbed contaminants are recovered from the steam condensate by extraction with an appropriate solvent. Infrared spectral analyses of contaminants desorbed from Hopenlite following its use as a catalyst for the reduction of rare compounds at various temperatures has provided a basis for ascertaining *ex post facto* the approximate operating conditions of a given catalyst bed. Steam elution of bulk catalyst provides a suitable method of salvaging explosively contaminated catalyst.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NR1, Project 001-9.

Project NR1-1000, Task NR 001-1000

SPECTROSCOPIC STUDIES OF NUCLEAR SUBMARINE ATMOSPHERES

I. Desorption and Analysis of Contaminants from Hopcalite

INTRODUCTION

The tremendous underwater cruising capability of the nuclear submarine has necessitated greatly improved methods for the maintenance of a livable atmosphere aboard the vessel. The complete problem of submarine respiratory habitability is a complicated one. One phase of the problem is the removal of any carbon monoxide or hydrogen generated in the boat's atmosphere. These contaminants can be removed by passing the air through a heated oxide catalyst known as Hopcalite. Hopcalite is a mixture of cupric oxide and manganese dioxide specially prepared to have a very large and active surface area. For this purpose it is used in the form of 4 to 8 mesh granules. It catalyzes the oxidation of carbon monoxide and hydrogen to carbon dioxide and water, respectively. It has been found that in addition to these compounds the catalyst also causes the oxidation of a number of organic contaminants in the boat's atmosphere to carbon dioxide and water vapor or to a lesser degree of oxidation depending upon the operating temperature of the catalyst bed. At the minimum temperature required for "burning" carbon monoxide and hydrogen, some of the organic contaminants in the entering air stream fail to react and are either adsorbed on the catalyst or discharged without change. Others are only partially oxidized, producing reaction products which may adsorb on the catalyst. Still others are oxidized completely to carbon dioxide and water vapor.

On several occasions these catalysts have produced low order explosions while in use aboard a submerged vessel. It is known that these explosions are triggered by a rise in temperature in the catalyst bed, or a part thereof, causing the desorption of some of the accumulated contaminants. The resulting rapid exothermic oxidation of these contaminants raises the catalyst temperature still higher causing further desorption, etc.

Several changes were made in the operating parameters of the catalytic burners shortly after the explosions to prevent future occurrences. The most important of these was to raise the operating temperature of the catalyst from about 125°C to 325°C, thereby increasing the rate and degree of oxidation, with a subsequent reduction in the amount of adsorbed material.

Samples returned from one of the nuclear submarines USS BRANWOLF, SS(N)575, however, were subjected to laboratory tests and found to explode at temperatures below the alleged operating temperature of the burners. It appeared desirable therefore to determine whether these so called "hot" catalysts were indeed formed at the usual operating temperature (325°C), resulted from a lower operating temperature, or resulted from adsorption caused

by the continued flow of air through the catalyst beds after burner shut-down. A laboratory method is therefore needed for ascertaining ex post facto the approximate operating conditions of the catalyst bed.

EXPERIMENTAL

The approximate conditions under which any given catalyst bed has been operated can probably be determined by analysis of contaminants adsorbed on the catalyst. Before such an analysis can be made, the adsorbed contaminants must be desorbed and separated from the catalyst. This operation is considerably more difficult than it might seem at first because of the explosive nature of the contaminated catalyst. The contaminants must be stripped without partial decomposition or without exploding the catalyst-contaminant mixture. Activated carbon adsorbents used in submarine air filters can be successfully desorbed by heating in vacuo and condensing the distillate. This method is undesirable in the case of the contaminated catalysts, however, because of their possible low explosion temperatures. Apparently the contaminants on Hopcalite are very tenaciously adsorbed. At temperatures up to 100°C nothing is desorbed by this method. Effecting the solution of Hopcalite in mineral acid and extracting the contaminants therefrom has been tried as a possible technique, but it is time consuming and yields unsatisfactory results. Another method of releasing the contaminants is to continuously filter a pure solvent through a column of the Hopcalite. After a period of time, dependent upon the relative affinity of the adsorbent for the solvent and each of the contaminants, the latter will be washed free from the adsorbent. This is known as elution. Almost any solvent for the contaminants will serve as an eluant although some are more effective than others. In general, the more polar the solvent the greater its affinity for the adsorbent and the less time and solvent is required to displace the contaminants. Most of the adsorbed contaminants on Hopcalite are probably oxidized to some degree and therefore highly polar. This type of compound is strongly adsorbed, and one should expect to use a strong (polar) eluant to displace them.

Some care must be exercised in choosing the solvent to be used as an eluant so that it does not react with the catalyst, thereby introducing spurious contaminants. Elution with ethyl alcohol, for instance, even at room temperature, results in the oxidation of some alcohol to acetic acid, which in turn reacts with the Hopcalite to produce acetates, making the identification of original contaminants difficult.

Based on the above considerations water appears as perhaps the best eluant. If water is used in the vapor state (as steam) its stripping power is increased several fold. Steam flowing down through the column of adsorbent tends to desorb the contaminants.

Those contaminants with a high affinity for the adsorbent displace those with a low affinity. The contaminants thus arrange themselves down the column in order of decreasing affinity for the adsorbent and are finally washed from the column in this order, i.e.; the eluted material is desorbed at varying rates of speed analogous to a liquid chromatogram. Steam has the added advantage of volatilizing some compounds which are insoluble in water thus increasing the range of the solvent, as it were. The degree to which the catalyst is stripped of contaminants by this method is not known. Low temperature explosive samples have been found to be drastically reduced in explosivity after a few minutes of elution however. There seems to be little likelihood of exploding the catalyst-contaminant mixture when using steam elution because the large volume of saturated steam and condensate flowing over the catalyst effectively controls its temperature.

A 50 gram sample of a typical low temperature explosive Hopcalite* was subjected to steam elution. Saturated steam was introduced at the top of a column, discharged from the bottom and passed through a water cooled condenser of sufficient length to cool the condensate to room temperature. The steam pressure at the top of the column was 9 psig. Several equal volume (50 cc) fractions were collected before stopping the elution. The desorbed contaminants were separated from the condensate by two or three successive extractions with an equal volume of an appropriate solvent(s). The contaminants obtained upon evaporation of the solvent were dissolved in carbon disulfide and examined in the 2 to 15 micron infrared spectral region. The solid residues obtained from the evaporation of the residual water were also examined in the same spectral region either as carbon disulfide solutions or as KBr pressed discs.

The infrared spectra of the various fractions (Figs. 1 and 2) indicated the presence of at least four or five different compounds, only one of which, benzoic acid, could be identified with certainty. Most of the contaminants contain the carboxyl group, however, and are probably organic acids. The compounds recovered from the residual water have spectra similar to those of metallic nectates. The concentration of some of the contaminants can be seen from the spectra to change progressively from fraction to fraction.

These compounds are the result of a very complicated mixture of atmospheric contaminants partially reacting on the catalyst. This simplifies the identification of the materials adsorbed on the catalyst.

- A low temperature explosive Hopcalite in a good catalyst form by laboratory tests to explode at a temperature below the recommended shipboard operating temperature (150°C). Some samples explode at temperatures considerably below this.

and to study the change in this material as the operating temperature of the catalyst is varied, it is preferable to limit the study to a single pure compound. Toluene was chosen as a representative aromatic compound for this purpose since it has previously been determined (by infrared analysis of the material desorbed from submarine filter carbon) to be the most prevalent aromatic in the submarine atmosphere. Air bubbled through toluene at 300 cc/min was passed for one hour through a bed of fresh catalyst maintained at a temperature of 115°C.* This temperature was selected as one slightly above the boiling point of toluene, but below the melting point of benzoic acid, the most likely reaction product. No effort was made to collect or analyze the effluent gases or vapors. The complete study of the reaction products formed by the combustion of various hydrocarbons on Hopenlite including gaseous products as well as the products adsorbed on the catalyst would be interesting and worthy of further investigation, but nonetheless, not germane to the immediate problem.

The reaction products adsorbed on the catalyst were removed by steam elution and examined spectrally. An expected benzoic acid was one of the products. Four or five other reaction products could be differentiated spectrally, but could not be identified. The spectrum of one of the unidentified reaction products is shown in Fig. 3. The spectrum of this compound has been compared without results with the spectra of all available compounds reported in the literature to result from the partial oxidation of toluene on oxide catalysts. The compound may be one not previously known to result from the partial oxidation of toluene.

Increasing the laboratory reaction temperature to 250°C resulted in the almost complete combustion of the toluene. Steam elution of the catalyst following combustion revealed very little adsorbed material. Condensants adsorbed on the catalyst as a result of high temperature combustion were present in much smaller quantity and were of a different character, spectrally, than those resulting from low temperature combustion.

The same conclusions may be drawn from a spectral comparison of low and high temperature combustion products of an aliphatic compound. Air bubbled through n-heptane at 300 cc/min was passed for one hour over Hopenlite at 115°C and again at 250°C and the condensants adsorbed on the catalyst in each case stripped and examined as previously described. It is interesting to note the formation of benzoic acid in the low temperature combustion of the heptane. Cyclization of the n-heptane occurred with the formation of toluene, which then oxidized to the acid. The aromatization

* This temperature is close to the operating temperature of the catalysts which produced the original shipboard explosions. The temperatures used for these analytical procedures, however, are unrelated to those recommended for shipboard operation.

n-heptane on chromium and molybdenum oxide catalysts is known to occur. Yields are excellent and the reaction is now an accepted industrial method for the preparation of toluene. Similar reactions involving other aliphatic hydrocarbons may possibly occur in the Hopenlite "CO burner" at least at this reduced temperature.

DISCUSSION

With this information it is now feasible to consider the problem at hand; namely, was or was not the low temperature explodable catalyst returned from SEA WOLF actually operated at a high temperature, as alleged. The entire sample returned from the ship amounted to about 75 grams. Fifty grams of this was used in the determination of the desired information. The minute quantity of adsorbed contaminants recovered from such a small sample qualifies this analysis as a micro-determination.

Steam elution of the subject sample yielded a cloudy condensate, which developed into a two phase system on standing. The clear off phase was essentially the same physically and spectrally similar to the oil* desorbed from samples of main filter carbon obtained from NAUTILUS. The water-soluble contaminants were similar in quantity and character to those resulting from high temperature combustion. These results indicate that the catalyst in question was indeed operated at high temperature, but also after burner shutdown, was allowed to remain in the air stream. During this time the cold catalyst acted as an adsorbent for atmospheric contaminants. Fortunately, this particular catalyst bed was not fired up again after shutdown. Future practice should ensure the prompt, perhaps automatic, removal of the catalyst bed from the air stream upon cessation of power to the catalyst heaters.

The effectiveness of steam elution for stripping contaminants from highly reactive adsorbents could be improved by increasing the steam pressure (temperature) and elution time. The low temperature explodable Hopenlite first discussed, which was steam eluted for a total of 30 minutes and dried in air at 200°C, was subsequently tested for explodability and found to be not dangerously explosive. Longer elution at higher temperature might have purged it completely.

* The latter has been spectrally identified as essentially paint thinner, i.e.; varsol. It may be desorbed from carbon either by heating in vacuo as previously mentioned or by steam elution.

Since present usage consumes about 100 pounds of catalyst (at \$7.00 per lb.) every 30 to 40 days, it is economically sound to consider methods for its salvage and reuse. A modification in the design of the "hydrocarbon incinerator" might well be considered in order that unexhausted but potentially dangerous catalyst might be purged and regenerated by complete steam elution.

CONCLUSIONS AND RECOMMENDATIONS

Steam elution is a satisfactory method for desorbing most contaminants from low temperature explosive oxide catalysts of the type described.

The approximate operating conditions of a Hopcalite catalyst used for the purification of submarine air can be determined *ex post facto*.

Under suitable conditions n-heptane can be aromatized to toluene over a Hopcalite catalyst.

Steam elution is recommended as a suitable means of salvaging unit sized batches of Hopcalite which have become explosively contaminated prior to the expiration of their normal useful life. Steam elution is also applicable to the recovery of activated charcoal saturated with hydrocarbon contaminant from the boat's atmosphere.

A more complete study of all the reaction products resulting from the partial oxidation of various pure compounds in the presence of Hopcalite at various temperatures would be interesting and worthy of further investigation.

LIST OF FIGURES

Successive Fractions (in Carb. D. 1111-13) of
A Low Temperature Explosive Hopanite

Pressed Disc Spectrum of a Commercial Benzene-soluble Explosive Hopanite

Unidentified Reaction Product (in Carb. D. 1111-13)
From the Partial Oxidation of Triphenyl Methyl

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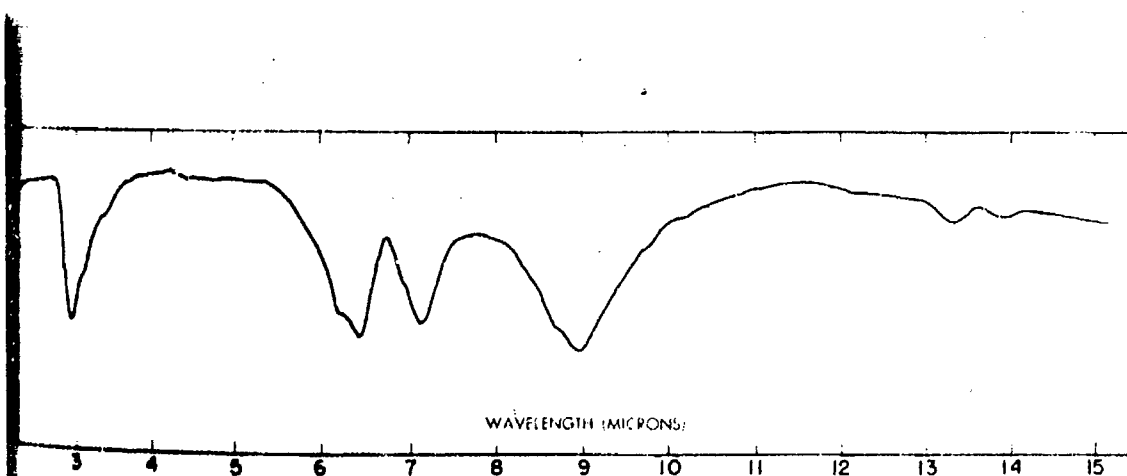


Figure 2 - Pressed Disc Spectrum of a Compound Desorbed from a Low Temperature Explosive Hopcalite

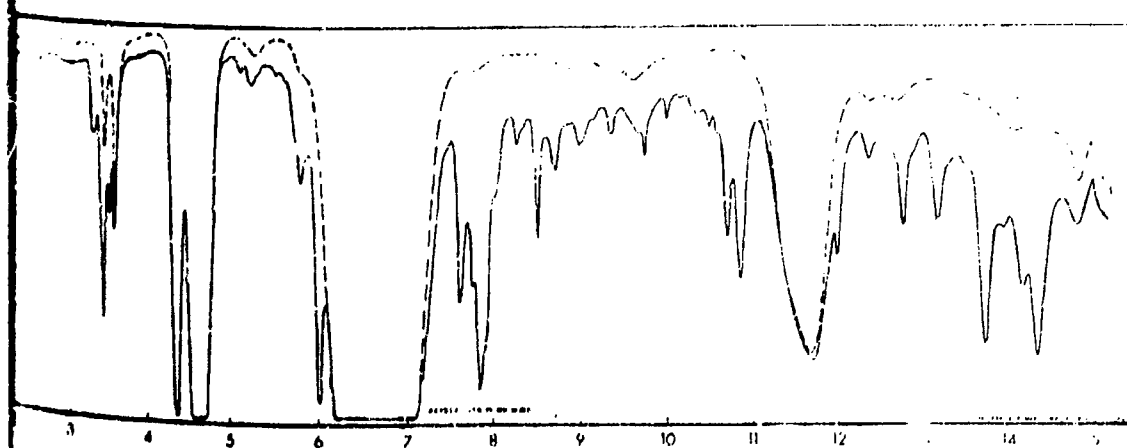


Figure 3 - Solid Line - Unidentified Reaction Product (in Carbon Disulfide Solution) from the Partial Oxidation of Toluene over Hopcalite Catalyst.

Dotted Line - Carbon Disulfide

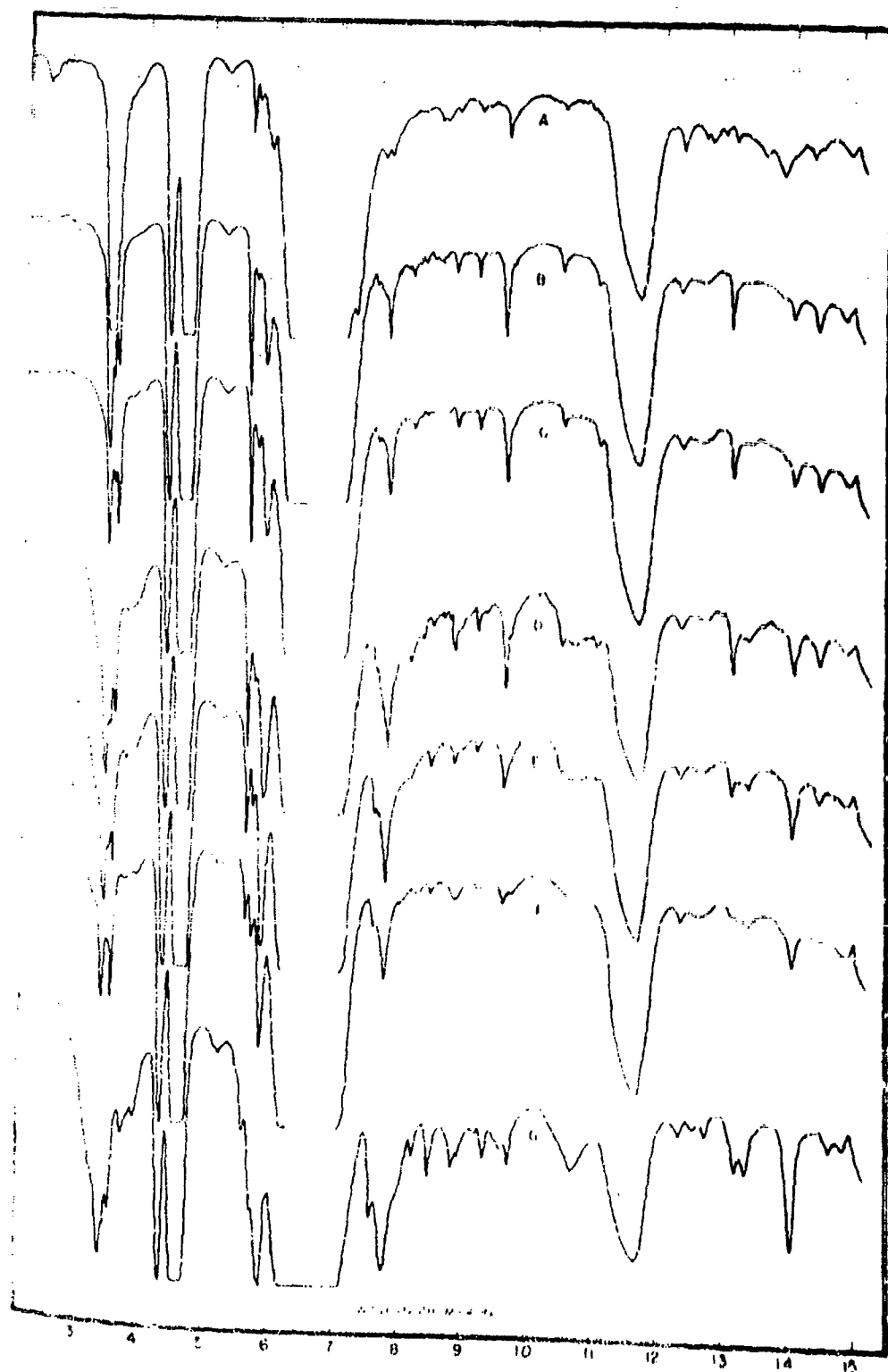


Figure 1 - Successive Fractions (in Carbon Disulfide Solution) Eluted from a Low Temperature Explosive Hopcalite