

A New Method for the Estimation of Dithiocarbamates using Vapodest

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Abstract: Dithiocarbamates are the products formed by the reaction between a primary or secondary amine with carbon disulfide in basic media. Such compounds have been widely used in analytical chemistry as complexing agents, fungicides, pesticides and insecticides in agriculture and presents a wide spread application in industry. The current methodology used by monitoring laboratories to determine dithiocarbamates in food involves the analysis of CS₂ generated after hydrolysis of the compound present in the sample. The use of vapodest for hydrolysis of dithiocarbamate and recover CS₂ showed good precision, accuracy and linearity. The Gas Chromatographic method was used for estimation of CS₂.

Key words: Dithiocarbamates, Vapodest, Gas Chromatograph, Carbon disulfide.

1. INTRODUCTION:

The ligands which are capable of complexing with metal ions have been incorporated into polymeric matrices to prepare ion exchange resins. Chelating ion exchange resins having specific chelating groups attached to a polymer back-bone have found extensive use in the separation of metal ions (1-6). The chelate forming polymeric ligands are characterized by reactive functional groups containing O,N,S and P donor atoms and capable of coordination to different metal ions have been studied(7-13). Dithiocarbamates are such group of compounds which are widely used in analytical chemistry as complexing agents, fungicides, pesticides and insecticides in agriculture. The complexing properties of dithiocarbamates are related to the presence of two electron donor sulfur atoms. In agriculture dithiocarbamates are a non-systemic group of pesticides widely used to protect crops from fungal diseases. However, these

dithiocarbamate biocides used may have harmful effect on environment. Hence it is necessary to control the dithiocarbamate residues in food stuffs. In analytical chemistry, the methodology most commonly used by monitoring laboratories to analyze dithiocarbamates is the detection of CS₂ generated after acid digestion of any dithiocarbamate present in the sample (14, 15). Spectrophotometry (16,17) or gas chromatography can be used for detection of these compounds. A method of detection for each specific dithiocarbamate compound is available (18, 19). In the Keppel method (20-25) dithiocarbamate samples were heated with a solution of stannous(II) chloride and hydrochloric acid yielding carbon disulfide. This is further distilled and passed through two absorption tubes- the first one contains a solution of lead acetate and the second a solution of sodium hydroxide. Carbon disulfide is then collected in the ethanol solution of cupric(II) acetate and diethanolamine. Two yellow cupric N,N – bis(2-

hydroxyethyl) dithiocarbamate complexes are formed and measured jointly by spectrophotometry. This method was improved (26) by determining the carbon disulfide formed during the heating of dithiocarbamates with the solution of stannous (II) chloride and hydrochloric acid in the head space by gas chromatography with electron capture detection or with flame-photometric detection in the sulfur mode. There is also another method in which the dithiocarbamate residue in fruit and vegetable samples are heated in a two phase system of isooctane/stannous (II) chloride in diluted hydrochloric acid. The carbon disulfide which is formed is dissolved in the organic phase (iso-octane) and determined by gas chromatography with mass selective detector. In the current method, we have made use of Gerhardt's Vapodest, an instrument designed for Kjeldahl digestion for the digestion of dithiocarbamate samples with stannous (II) chloride and hydrochloric acid.

2. MATERIALS AND METHODS:

2.1 Chemicals and materials:

Acrylamide (SRL), acrylic acid (Rolex) and potassium persulfate (Ranbaxy) were used for polymerization without any prior purification.

Sodium diethyl dithiocarbamate of purity 97% from Loba was used for recovery study. Ethyl alcohol solution of purity 99.9% was obtained from Merck. Carbon disulfide solution of 99.0% purity was obtained from Merck.

2.2 Sample preparation:

To estimate dithiocarbamate content in the samples, initially we have prepared water soluble polymeric dithiocarbamates. Simple homopolymers and copolymers of Acrylamide and Acrylic Acid were prepared at different feed ratios as outlined by Rakshit et al (27). Then a mixture of 5g of the synthesized polymer, 25ml of ethanol and 10ml of water were kept for two days at room temperature. 6g of NaOH was dissolved in 100ml of water and added to the above mixture slowly with continuous stirring. The contents were cooled below 10°C and added 10ml of CS₂. The mixture was stirred intermittently till CS₂ layer completely disappeared. An orange coloured resinous polymeric dithiocarbamate was separated out after addition of acetone which was washed with water, followed by ethanol and dried in a desiccator. The same procedure was followed for dithiocarbamation of other copolymers also. Now the sample is ready for Vapodest distillation.

Preparation of SnCl₄ solution:- 20g stannous (II) chloride dehydrate were dissolved in 500mL concentrated hydrochloric acid (35%-37%); the solution was decanted into a one-litre volumetric flask and filled to the designated mark with distilled water.



VAPODEST watersteam rapid distillation system is designed for Kjeldahl digestion, determination of nitrate, nitrite, ammonium, volatile acids etc. In the present case we made use for the determination of dithiocarbamation as explained below:

In this case, a known quantity of the polymeric dithiocarbamate is taken in the Kjeldatherm digestion tube of the Vapodest. Added 100ml of SnCl₄ solution to the tube. Then the tube was mounted onto Vapodest and started steam digestion at a lower pressure for 15 minutes. The steam vapor is collected in a 250ml volumetric flask. After 10 minutes, ethanol was added for 3 minutes through the NaOH addition tube of the vapodest. The distillation continued for another 7 minutes and the distilled component which contains carbon disulfide was collected. The distilled component contains carbon disulfide, ethanol and water. To inject the sample into Gas Chromatograph, the water component needs to be removed. Hence another 50ml of ethanol was added to the distillate and the whole quantity of the distillate was added to another Kjeldatherm tube and distilled out for 7 minutes at a digestion rate of 70. Now the distillate contains ethanol and a small portion of water along with carbon disulfide. This sample is ready to inject into GC.

2.3 Estimation: Standard carbon disulfide solutions were prepared in ethanol and injected into GC which is maintained under the conditions given below:

- a. Injector temperature: 200°C

- b. FPD Detector temperature: 210⁰C
- c. Auxiliary temperature: 200⁰C
- d. Oven: 60⁰C for 10 minutes, then at a rate of 5.0⁰ C/minutes reach 195⁰C and hold for 5 minutes
- e. Flow: 0.5ml/min
- f. Column:Quadrex 007-FFAP 0.25 mm i.d., 50 m length.

A linear graph of the log(conc)² vs. log(area) was plotted. Afterwards, the above prepared samples were injected into GC and the concentration was determined.

The above method was validated using standard sodium diethyl dithiocarbamate of known purity. This standard was treated in the same way as that of the sample. Recovery was calculated for triplicate samples.

3. RESULTS AND DISCUSSION:

Linearity was verified by using the solutions of carbon disulfide in ethanol, five repetitions for one concentration level. Linearity and range were determined by linear regression. For checking the

recoveries, standard diethyl dithiocarbamate solution was treated in the same way as that of the sample. Triplicate samples were used for recovery. The sample concentrations are expressed as the percentage of sulfur in the given sample which is as tabulated below:

Name of the compound	% Sulfur
Dithiocarbamate of 100 % Acrylamide	20.3
Dithiocarbamate of AA:AAc(85:15)	17.2
Dithiocarbamate of AA:AAc(65:35)	12.8
Dithiocarbamate of AA:AAc(50:50)	11.2

AA= AcrylamideAAc= Acrylic acid

4. CONCLUSION:

Based on the recovery results, the method is found to be suitable for determination of dithiocarbamate concentration in the given sample.

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