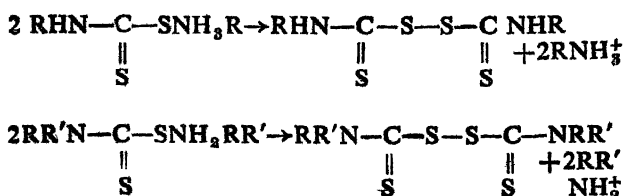


From the volume of iodine or iodine halide solution used corresponding to the equivalence point in visual and potentiometric titrations, the amount of each compound was calculated. The results of determination of the compounds with iodine monobromide (as a representative of these oxidants) are given in Table 1. Since the results obtained by potentiometric titrations using platinum-modified calomel electrode assembly agree closely with those obtained with platinum-antimony electrode assembly, hence for sake of convenience, only the former are recorded in the Table. The inflection points and potentials jumps corresponding to each compound are also recorded in the Table.

### Results and Discussion

The determination of alkyl / arylammonium alkyl / arylthiocarbamates with iodine or iodine halides is based on their oxidation to the corresponding substituted thiuram disulphides.



R, R' = alkyl or aryl group (same or different)

The results obtained for the determination of these compounds with iodine and iodine halides agree so well among themselves that it would be appropriate to mention the results with one of the oxidant only. Results with iodine monobromide are recorded in Table 1. The overall standard deviation calculated from the pooled data of all the visual and potentiometric titrations performed with 10 mg of each dithiocarbamate have been found to be 0.035 and 0.029 respectively. The same for 40 mg samples are 0.075 and 0.052 respectively. The potential jump at the equivalence point in titrations of dithiocarbamates with iodine monobromide in acetonitrile medium using platinum-modified calomel electrode assembly have been found to be of the order of 240 to 330 mV with the addition of 0.05 ml of 0.05 N oxidant solution. Using platinum-antimony electrode assembly, the jump in potential is of the order of 270 to 375 mV with the addition of 0.05 ml of 0.05 N oxidant solution.

The effect of some typical compounds in the titrations of alkyl/arylammonium alkyl/aryldithiocarbamates with iodine and iodine halides was studied by the recommended procedure in the usual way. No interferences were found from alkyl isothiocyanates, isocyanates, urea and carbon disulphide even when present in upto 6-fold amounts relative to dithiocarbamate. Amines, thioacetamide and mercaptans interfered.

### Acknowledgement

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### Solvent Extraction and Spectrophotometric Determination of Zinc with Thiobenzoylacetone

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**A**CETYLACETONE<sup>1-3</sup> proved to be an inefficient extractant for zinc, while benzoylacetone and dibenzoylmethane<sup>4</sup> extracted it from highly alkaline media. 2-Thenoyltrifluoroacetone<sup>5</sup> and thiothenoyltrifluoroacetone<sup>6</sup> and thenoyltrifluoroacetone in presence of tributyl phosphate<sup>6</sup> were also used for the extraction of zinc. Thiothenoyltrifluoroacetone<sup>7</sup> and thiodibenzoylmethane<sup>8</sup> when used as extractants, improved the selectivity to some extent. This paper presents a better method for the extractive spectrophotometric determination of zinc with thiobenzoylacetone.

### Experimental

**Apparatus:** Spektromom-204 spectrophotometer with matched 10 mm quartz cells. Digital pH meter (ECIL, India), pH-822 model with glass and calomel electrodes. Wrist action flask shaker (Toshniwal and Co., India).

**Reagents:** Thiobenzoylacetone (HSBA) was synthesised from benzoylacetone (Fluka, England) as per the procedure described earlier<sup>9</sup>. A  $5 \times 10^{-4}$  M solution in benzene was used and was always preserved in a refrigerator.

A stock solution of zinc was prepared by dissolving 5.50 g. of zinc sulphate heptahydrate (BDH, AnalaR) in 250 ml. of distilled water. The solution on standardization complexometrically<sup>10</sup> was found to contain 5 mg./ml. of zinc. A dilute solution containing 2  $\mu$ g./ml. of zinc was prepared by appropriate dilution.

A buffer solution of pH 7.7 was prepared by mixing 91 ml. of 0.06 *M* disodium hydrogen phosphate and 9 ml. of 0.06 *M* potassium dihydrogen phosphate.

A buffer solution of pH 12.0 was prepared by mixing 100 ml. of 0.05 *M* borax and 126.5 ml. of 0.1 *M* sodium hydroxide solutions.

**General Procedure:** An aliquot of solution containing 0.5–16  $\mu\text{g}$  of zinc was taken. Ten ml. of buffer solution of pH 7.7 were added and the solution was diluted to 25 ml. with distilled water. It was transferred to a separatory funnel and was shaken for 5 min., with 10 ml. of  $5 \times 10^{-4}$  *M* thiobenzoylacetone in benzene, on the wrist action flask shaker. After allowing the layers to settle and separate, the aqueous phase was removed. In order to remove the excess reagent from the organic phase, the yellow coloured organic phase was shaken with 10 ml. buffer solution of pH 12.0 for about 2 min. The alkaline aqueous phase was removed and the organic phase was transferred to a 10 ml. volumetric flask. The absorbance of the complex was measured at 390 nm, against the reagent blank prepared similarly. The amount of zinc was computed from the calibration curve.

## Results and Discussion

**Absorption spectra:** The absorption spectrum of zinc-thiobenzoylacetone complex against the reagent blank is shown in Fig. 1. The yellow coloured complex showed absorption maximum at 390 nm. The molar absorptivity of the complex is  $3.7 \times 10^4$  l. mole<sup>-1</sup>. cm<sup>-1</sup> and the sensitivity is  $1.9 \times 10^{-4}$   $\mu\text{g}$ . cm<sup>-2</sup>.

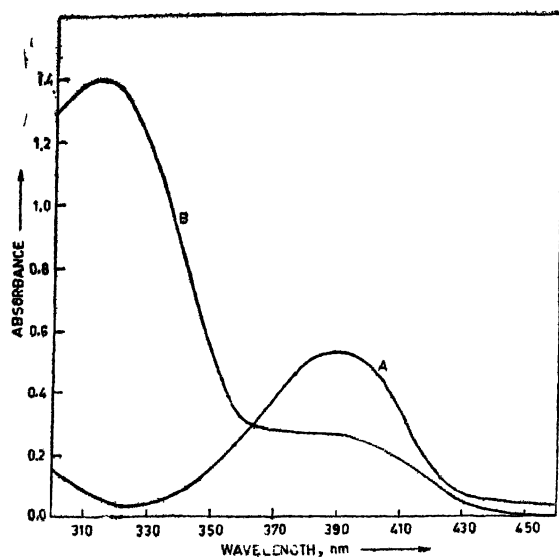


Fig. 1

**Effect of pH:** Extraction studies of zinc in the pH range of 1 to 10 showed that extraction was quantitative in the pH region of 6.8–8.6. There was no extraction below pH 5.0 and above pH 9.0.

**Beer's Law:** The extraction of varying amount of zinc, from 0.05 to 1.6  $\mu\text{g}/\text{ml}$ . at pH 7.7 showed that the Beer's law is valid over the concentration range of 0.05–1.6  $\mu\text{g}/\text{ml}$ . of zinc, at 390 nm. The optimum metal concentration range as evaluated by Ringbom plot<sup>11</sup> was 0.4 to 1.6  $\mu\text{g}$  of zinc per ml.

**Stability of the complex:** The absorbance of the zinc-thiobenzoylacetone complex was stable for 48 hr, beyond which it started showing decrease in absorbance.

**Effect of reagent concentration:** Zinc was extracted with varying concentration ( $1.0 - 20 \times 10^{-4}$  *M*) and volumes (2.5–20 ml. of  $5 \times 10^{-4}$  *M*) of the reagent. The extraction was quantitative with 10 ml. of  $5 \times 10^{-4}$  *M* reagent. The extraction was incomplete with smaller volumes and smaller concentrations of the reagent, whereas the higher reagent concentration showed no significant enhancement in the extraction.

**Effect of salting-out agents:** The sulphates of ammonium, sodium, lithium, potassium and magnesium in the concentration range of 0.5–2.0 *M* when used as salting-out agents, showed no effect on the process of extraction.

**Effect of Diverse Ions:** The tolerance limit was set as the amount of the foreign ion, in presence of which the error in the recovery of zinc is  $\pm 2\%$  (Table 1).

TABLE 1—EFFECT OF DIVERSE IONS

Zn=0.01 mg; pH=7.7; (HSBA)= $5 \times 10^{-4}$  *M* in benzene

Tolerance limit, mg.	Foreign Ions
50	NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Li <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup> , Sr <sup>2+</sup> , Cl <sup>-</sup> , F <sup>-</sup> , I <sup>-</sup> , Br <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , SO <sub>3</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , CO <sub>3</sub> <sup>2-</sup> , SCN <sup>-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , ascorb <sup>-</sup> , tartarate <sup>-</sup> , acetate <sup>-</sup> .
30	Thiourea, mal <sup>2-</sup> .
10	Cs <sup>+</sup> , Rb <sup>+</sup> , UO <sub>2</sub> <sup>2+</sup> , Mo <sub>7</sub> O <sub>4</sub> <sup>2-</sup> .
5	Be <sup>2+</sup> , Te <sup>4+</sup> , VO <sub>2</sub> <sup>+</sup> , ReO <sub>4</sub> <sup>-</sup> , CrO <sub>4</sub> <sup>2-</sup> , AsO <sub>4</sub> <sup>3-</sup> , Th <sup>4+</sup> , Zr <sup>4+</sup> , Y <sup>3+</sup> , Ge <sup>4+</sup> , Ga <sup>3+</sup> , Ti <sup>4+</sup> .
2	WO <sub>4</sub> <sup>2-</sup> , Ti <sup>4+</sup> , In <sup>3+</sup> .
1	SeO <sub>3</sub> <sup>2-</sup> , Sc <sup>3+</sup> , Ce <sup>4+</sup> , Pt <sup>4+</sup> .
0.5	Fe <sup>3+</sup> , Ru <sup>3+</sup> , Ag <sup>+</sup> .
0.2	Bi <sup>3+</sup> , Ir <sup>3+</sup> , Os <sup>3+</sup> , Au <sup>3+</sup> , Pd <sup>2+</sup> , Cu <sup>2+</sup> , Hg <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> .
None	Cd <sup>2+</sup> , Mn <sup>2+</sup> , Rh <sup>3+</sup> , CN <sup>-</sup> , Cit <sup>3-</sup> , EDTA <sup>4-</sup> .

Alkali, alkaline earths, common anions and anions of organic sequestering agents were tolerated in ratios exceeding 5000:1. Cadmium, manganese, rhodium, cyanide, citrate and EDTA showed strong interference. The interference of some of the ions were eliminated using masking agents as shown in parantheses;

e.g. beryllium, zirconium(IV) and germanium (sodium fluoride); thorium, scandium, indium(III) and bismuth (ascorbic acid); yttrium, titanium, gallium and cerium(IV) (tartaric acid) and silver (thiourea). The interferences of some of the ions were removed by prior extraction with suitable extractants (1) as shown in brackets; gold (diethyl ether), cobalt (1-nitroso-2-naphthol), nickel (dimethylglyoxine), lead (2-thenoyl-trifluoroacetone) and palladium, copper(II) and mercury(II) (thiobenzoylacetone).

From ten determinations with 10  $\mu$ g. of zinc, the absorbance was  $0.530 \pm 0.01$ . The standard deviation was  $\pm 1.03\%$ .

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### Kinetic Evidence for Steric Enhancement of Resonance\*\*

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THE phenomenon of steric enhancement of resonance was discovered by Baliah and Uma<sup>1</sup> while studying the electric dipole moments of some substituted anisoles and acetophenones. The results obtained from our present studies of the kinetics of oxidation of some

substituted phenyl methyl sulphoxides with chloramine-T support this concept.

### Experimental

Chloramine-T used was of AnalaR grade (BDH). The purity of each compound was tested by TLC. The kinetics of the reaction was followed by iodometric estimation of chloramine-T in a measured aliquot of the reaction mixture at various time intervals. Phenyl methyl sulphone was found to be the reaction product polarographically.

### Results and Discussion

The kinetic data for the oxidation of phenyl methyl sulphoxides with chloramine-T are given in Table 1. *p*-Methoxyphenyl methyl sulphoxide undergoes oxidation 3.1 times faster than phenyl methyl sulphoxide.

TABLE 1—OXIDATION OF PHENYL METHYL SULPHOXIDES BY CHLORAMINE-T IN BUFFERED ETHANOL (1:1 v/v; pH=7.3)

Substrate	$k_2 \times 10^3$ 1. mol <sup>-1</sup> sec <sup>-1</sup>
Phenyl methyl sulphoxide	4.34
3-Tolyl methyl sulphoxide	5.99
4-Methoxyphenyl methyl sulphoxide	13.45
4-Methoxy-3-methylphenyl methyl sulphoxide	20.54
4-Methoxy-3,5-dimethylphenyl methyl sulphoxide	8.80

*m*-Tolyl methyl sulphoxide also undergoes oxidation 1.4 times faster than phenyl methyl sulphoxide. The rate of oxidation of 4-methoxy-3-methylphenyl methyl sulphoxide is significantly higher than that of 4-methoxyphenyl methyl sulphoxide. This increase in rate is not solely due to the 3-methyl group, because the observed rate constant of 4-methoxy-3-methylphenyl methyl sulphoxide ( $20.54 \times 10^{-2}$  1 mol<sup>-1</sup> sec<sup>-1</sup>) is 11% higher than the value ( $18.57 \times 10^{-2}$  1 mol<sup>-1</sup> sec<sup>-1</sup>) predicted on the basis of additivity principle<sup>2</sup>. This appreciable difference between the observed and the calculated rate is significant because 3-methyl group does not sterically inhibit the resonance interaction of the *p*-OCH<sub>3</sub> group with the aromatic ring but enhances it. This can be explained by assuming a trans orientation of the methoxy group to the 3-methyl group increasing the probability of its attaining planarity with the aromatic ring due to restricted rotation.

If a single substituent ortho to the -OCH<sub>3</sub> group enhances its resonance interaction with the para substituents, two ortho substituents should cause steric inhibition of resonance, because the two ortho substituents will prevent the -OCH<sub>3</sub> group from attaining planarity with the benzene ring and hinder conjugation with the ring. A comparison of the rate constant calculated for 4-methoxy-3, 5-dimethylphenyl methyl

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