Asian Journal of Chemistry; Vol. 29, No. 1 (2017), 76-80

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2017.20135

Trace Determination of Tin(II) Using 6-Chloro-3-hydroxy-2-{(E)-1'-methyl-2'-phenylvinyl}-4-oxo-4*H*-1-benzopyran as Analytical Reagent

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Received: 13 June 2016; *Accepted*: 18 September 2016; *Published online*: 29 October 2016; AJC-18101

6-Chloro-3-hydroxy-2-{(*E*)-1'-methyl-2'-phenylvinyl}-4-oxo-4*H*-1-benzopyran (CHMPB) solution in ethanol forms a yellow coloured (1:1) complex with tin(II) in hydrochloric acid medium which is extractable into dichloromethane after equilibration. During study on this complex, it is found to be quite stable, obeying Beer's law. Interaction is studied with various ions and molar absorptivity, Sandell's sensitivity, standard deviation, regression coefficient, linear regression equation and detection limit are also investigated. Job's method and mole ratio method are used to study stoichiometry of the complex. The method is simpler, more accurate, sensitive, rapid and selective as compared to existing methods and is applicable to analysis of various synthetic samples of varied composition and industrial sample like gun metal.

Keywords: Tin(II), 6-Chloro-3-hydroxy-2-{(E)-1'-methyl-2'-phenylvinyl}-4-oxo-4*H*-1-benzopyran, Spectrophotometric determination.

INTRODUCTION

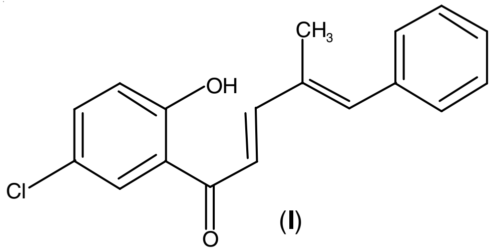
Determination of tin is widely required because of its harmful and toxic nature and its various applications in different industries [1,2]. A number of techniques [3-7] have been used for the purpose including spectrophotometry [2,8-15]. In continuation of our work on the spectrophotometric determination of metal ions, an attempt has been made to introduce a new benzopyran derivative, 6-chloro-3-hydroxy-2-{(E)-1'-methyl-2'-phenylvinyl}-4-oxo-4*H*-1-benzopyran (CHMPB) for complexation and extractive determination of tin which not only gives high sensitivity but also offers the advantages of high selectivity and rapidity as compared to most of the existing methods of determination of tin in its +2 and +4 oxidation state [2,8-15].

EXPERIMENTAL

A UV-visible spectrophotometer with 10 mm matched glass cells was used for absorbance measurement and spectral studies.

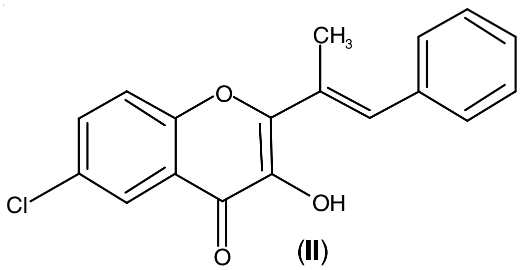
Synthesis: 6-Chloro-3-hydroxy-2-{(E)-1'-methyl-2'-phenylvinyl}-4-oxo-4*H*-1-benzopyran [16] (m.p. 138-140 °C) was prepared by a two step reaction as discussed below:

Synthesis of 1-(5'-chloro-2'-hydroxyphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (I): A solution of 2-hydroxy-5-chloroacetophenone (17 g, 0.1 mol) and α-methylcinnamaldehyde (14.6 g, 0.1 mol) in ethanol and dehydrated S-200 $Ba(OH)_2$ (20 g) were refluxed on water bath for 20 min. The solution was cooled and poured into crushed ice; it was then acidified with conc. HCl to give yellow solid. The solid was filtered, washed with water and crystallized from ethanol to give product (**I**). Yield: 24 g (80 %), light yellow solid, m.p. 96-98 °C.



(I)

Synthesis of 6-chloro-3-hydroxy-2-{(E)-1'-methyl-2'-phenylvinyl}-4-oxo-4*H*-1- benzopyran: A solution of **I** (2.98 g, 0.01 mol) in methanol at 0 °C was mixed with powdered NaOH (1.4 g, 0.35 mol). To this dark red solution was added H_2O_2 (50 % w/v) dropwise with stirring till the colour changed to yellow. This solution was warmed to 40 °C for 10 min and poured into ice-HCl to give light yellow precipitate. The solid was filtered, dried and crystallized (chloroform-ethanol) to give greenish yellow crystals. Yield: 1.25 g (42 %), m.p. 138-140 °C.



(II)

A stock solution of tin(II) containing 1 mg mL^{-1} of the metal ion was prepared by dissolving an accurately weighed amount (0.190 g) of $SnCl_2 \cdot 2H_2O$ (CDH) in 8 mL of concentrated hydrochloric acid , diluting with deionized water upto the mark and standardized by SnO_2 method gravimetrically [17]. Lower concentrations of µg mL^{-1} level were prepared by appropriate dilution of this solution. The containers of tin solution were wrapped with carbon paper and kept in dark. At the mg mL^{-1} level, stock solutions of other metal ions were prepared by dissolving their sodium or potassium salts in deionized water or dilute acids and standardized by appropriate methods [17]. At the µg level these solutions were appropriately diluted to obtain lower concentration of the metal ion.

A stock solution of 6-chloro-3-hydroxy-2-{(E)-1'-methyl-2'-phenylvinyl}-4-oxo-4*H*-1-benzopyran (CHMPB) was prepared by dissolving a sample in ethanol to give a 0.2% w/v solution. Hydrochloric acid, 1 M was prepared by diluting 12 M hydrochloric acid (CDH, AR) in deionized water. Dichloromethane (CDH, AR) was used as such for extraction.

Determination of tin(II): An aliquot of the sample solution containing upto 33 µg of Sn(II) and other ions was taken in a 25 mL beaker. To this, 0.3 mL of 1M HCl and 1 mL of 0.2 % (w/v) CHMPB were added. The whole mixture was diluted to 10 mL with deionized water to bring the final acidity of the aqueous phase 0.03 M. The contents were gently mixed and heated upto 50 °C, cooled and transferred to a 125 mL separatory funnel. The yellow coloured organic layer was filtered through a Whatman filter paper no.41 (9 cm diameter, pretreated with dichloromethane) into a 10 mL volumetric flask. The absorbance of the yellow complex was measured at 417 nm against similarly treated reagent blank. The tin content was determined from the calibration curve prepared under identical conditions of the proposed procedure.

RESULTS AND DISCUSSION

CHMPB reacts with tin(II) in hydrochloric acid medium to give a yellow coloured stable complex extractable into dichloromethane quantitatively. In other acids such as acetic acid, nitric acid, perchloric acid, sulphuric acid and phosphoric acid, the colour observed was less intense with a lower value of absorbance in the same order. Therefore, HCl medium was preferred for further studies.

The optimum values of other parameters found for achieving maximum and constant absorbance of the coloured complex were: 0.02-0.05 M HCl, 0.8-1.5 mL of 0.2% CHMPB solution in ethanol and 45-52 °C temperature for 0-3.3 µg of Sn(II) mL^{-1} aqueous solution and equilibrating with 10 mL of dichloromethane once over the time period of 5-120 s (Table-1).

Choice of extractant: Various solvents have been tested as extractant for the coloured metal complex. The extraction varies in the following order: dichloromethane, chloroform, 1,2-dichloroethane, carbon tetrachloride, toluene, carbon disulphide, *n*-butyl acetate, isobutyl methyl ketone, isoamyl alcohol, ethyl acetate, benzene and cyclohexane. In dichloromethane, the absorbance remains unchanged for more than 0.5 h. Hence, dichloromethane is preferred as an extractant for the metal complex. The coloured complex of Sn(II) with CHMPB developed at 0.03 M HCl is completely transferred into the organic layer in one extraction step.

Optical characteristics: The absorption spectra of Sn(II)-CHMPB complex in dichloromethane indicated that maximum of the complex lied in the range of 407-422 nm where the reagent blank also showed some absorbance (Fig. 1). Beer's law was obeyed in the concentration range of 0-3.3 µg Sn(II) mL^{-1}. However, the optimum range of determination as evaluated from the Ringbom plot [18] (a plot between log ppm of tin and % transmittance) was 0.22-3.16 ppm. The molar absorptivity and Sandell's sensitivity of the complex were 4.876×10^4 L mol^{-1} cm^{-1} and 0.00244 µg Sn(II) cm^{-2}, respectively at 417 nm. The linear regression equation was $y = 0.412x - 0.008$ (y = absorbance, x = µg Sn(II) mL^{-1}) with correlation coefficient, r = 0.9975. The detection limit of the method was 0.26 µg mL^{-1} (Table-2).

Stoichiometry of complex: Equimolar solutions of tin and CHMPB at two different concentrations (8.424×10^{-4} M

TABLE-1
EFFECT OF VARIOUS PARAMETERS ON THE ABSORBANCE OF Sn(II) COMPLEX

HCl (M)^a	0.01	0.02-0.05	0.06	0.07	0.08				
Absorbance	0.516	0.630	0.600	0.516	0.500				
Temperature (°C)^b	28	40	45-52	54	60				
Absorbance	0.630	0.685	0.720	0.690	0.620				
0.2 % CHMPB (mL)^c	0.2	0.4	0.7	0.8-1.5					
Absorbance	0.290	0.375	0.390	0.410					
Equilibration time (s)^d	2	5-120							
Absorbance	0.251	0.410							
Sn(II) (µg mL^{-1})^e	0.2	0.6	1.0	1.4	1.8	2.0	3.0	3.3	3.5
Absorbance	0.080	0.272	0.410	0.545	0.693	0.797	1.302	1.330	1.340

^{a}Sn(II) = 20 µg, HCl = variable, 0.1 % (w/v) CHMPB in ethanol = 0.5 mL, equilibration time = 30 s, solvent = dichloromethane, aqueous phase = organic phase = 10 mL, number of extractions = 1; ^{b}HCl = 0.03 M, other conditions as in (a) except for the variation in temperature; ^{c}Temperature = 50 °C, Sn(II) = 10 µg, other conditions as in (b) except for the variation in CHMPB concentration; ^{d}0.2 % (w/v) CHMPB in ethanol = 1 mL, other conditions same as in (c) except for the variation in equilibration time; ^{e}Equilibration time = 30 s, other conditions same as in (d) except for the variation in tin concentration.

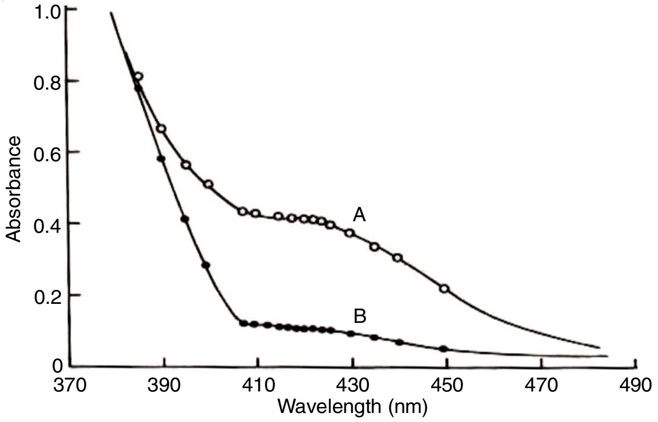


Fig. 1. Absorption spectrum of Sn(II)-CHMPB complex in dichloromethane. Curve A = 10 μg Sn(II) mL^{-1} measured against reagent blank; curve B = Reagent blank measured against pure dichloromethane; HCl = 0.03 M; CHMPB (0.2 % w/v) = 1 mL

TABLE-2
OPTICAL CHARACTERISTICS OF THE PROPOSED METHOD

Parameter	Value
λ_{max} (nm)	407-422
Beer's law (μg Sn(II) mL^{-1})	0.0-3.3
Molar absorptivity (L mol^{-1} cm^{-1})	4.867×10^4
Sandell's sensitivity (μg Sn(II) cm^{-2})	0.00244
Correlation coefficient	0.9975
Optimum detection range (μg Sn(II) mL^{-1})	0.22-3.16
Detection limit (μg mL^{-1})	0.26
Standard deviation	0.0014
Relative error (%)	0.244

and 2.106×10^{-4} M) were utilized to determine metal to ligand ratio by Job's method of continuous variations [19] as modified by Vosburgh and Cooper [20]. The obtained curves were indicative of 1:1 stoichiometry in the extracted species (Figs. 2 and 3). This was further confirmed using the mole ratio method [21] by taking fixed concentration of tin as 2.106×10^{-4} M, varying the reagent concentration and measuring the absorbance at 3 different wavelengths as 417, 430 and 450 nm (Fig. 4).

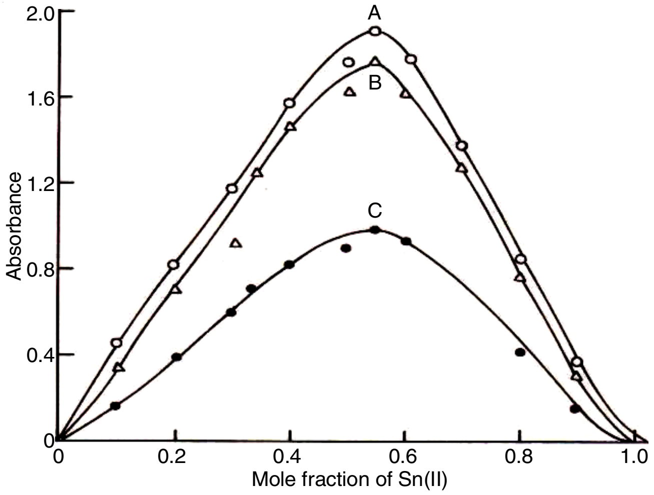


Fig. 2. Job's method of continuous variations. Total concentration: Tin + CHMPB = 8.424×10^{-4} M; curve A = 417 nm, curve B = 430 nm, curve C = 450 nm, HCl = 0.03 M

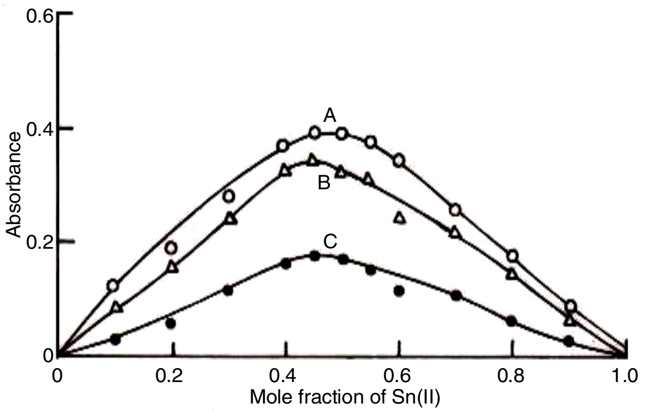


Fig. 3. Job's method of continuous variations. Total concentration: Tin + CHMPB = 2.106×10^{-4} M, curve A = 417 nm, curve B = 430 nm, curve C = 450 nm, HCl = 0.03 M

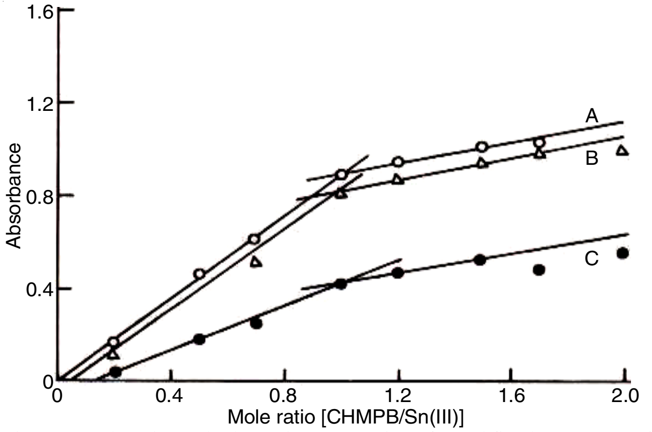
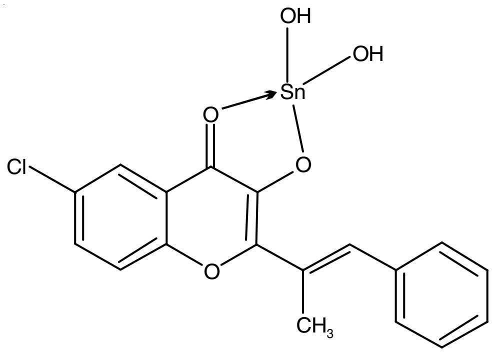


Fig. 4. Mole ratio method. Total concentration of metal fixed; [Sn] = 2.106 × 10^{-4} M; curve A = 417 nm, curve B = 430 nm, curve C = 450 nm, HCl = 0.03 M

The probable structure of yellow coloured tin(II)-CHMPB complex in dichloromethane is assigned as below:



[Sn(II)-CHMPB complex]

Effect of diverse ions: The effect of various ions taken in quantities as maximum amounts causing less than 1 % error was studied in presence of 10 μg Sn(II)/10 mL under the optimum conditions of the proposed procedure (amounts in mg/10 mL are shown in parenthesis): iodide (100); nitrate, sulphate, thiourea, sulphite, bromide and thiocyanate (50 each); ascorbic acid (30); chloride, acetate and nitrite (10 each); citrate (5); dithionite and phosphate (1 each); disodium 'EDTA' (0.05) and glycerol and 30 % H_2O_2 (0.5 mL) caused 1 % error. However, even in trace amounts, oxalate and fluoride interfered seriously with the procedure.

Among the various cations (also taken in maximum amounts causing < 1 % error) studied which do not interfere at all are: Zn(II), Mn(II), Ca(II) and Cu(II) (10 each); Co(II), Cd(II), Mg(II) ,Ba(II) and Pb(II), Hg(II) and Ni(II) (8 each); Se(IV) and Sr(II) (5 each); As(III), Ag(I) and Cr(VI) (1 each); Al(III) (0.8); Os(VIII), Ta(V) and Th(IV) (0.5 each); Fe(III) (0.3); Re(VII), Ru(III) and Zr(IV) (0.1 each); Ir(III), Pd(II), Pt(IV) and Au(III) (0.05 each).

Vanadium(V) (0.5) and Ce(IV) (0.1) were masked with ascorbic acid (30 mg); W(VI) (0.5) and Mo(VI) (0.1) with 30 % H_2O_2 (0.5 mL); Ti(IV) (0.1) with phosphate (1 mg) and Nb(V) (0.1) with sodium dithionite (1 mg).

Determination of tin in synthetic mixtures and gun metal: Synthetic samples (some of them analogous to tungsten brass, aluminium tin bronze, ceco alloy, magnalium cast Z, kneiss metal and argental) were prepared by mixing the solutions of various metal ions in appropriate proportions and analyzed satisfactorily to check applicability of the method (Table-3).

Gun metal sample: A weighed sample of gun metal (0.2 g) was dissolved in 10 mL of concentrated HCl and 2-3 mL of concentrated HNO_3 on heating. The volume was made upto 100 mL in volumetric flask. 10 mL of this solution was further diluted to 100 mL to get a working solution of low concentration. Tin(II) was then analyzed by the proposed method by taking suitable aliquots.

Analytical applications: For microdetermination of Sn(II), the proposed method is highly sensitive and free from the interference of a large number of metal ions including platinum metals and also the elements such as vanadium, chromium, iron, cobalt, nickel, copper, molybdenum, zirconium, niobium and rhenium. Usefulness of the method is further been tested by carrying out the analysis of a wide variety of samples containing different amounts of tin and other metal ions (Table-3). The result obtained by the proposed method is accurate with a standard deviation of ± 0.0014 for 10 replicates containing 1 µg Sn(II) mL^{-1} each time. The proposed method is superior to the existing methods in respect of sensitivity, selectivity and rapidity (Table-4).

TABLE-3
ANALYSIS OF Sn(II) IN SYNTHETIC AND REAL SAMPLES BY THE PROPOSED METHOD

Composition of sample	Sn(II) µg	
	Added	Found**
Cu (4.0), Zn (2.0), Al (0.1)	25	26.8
Ba (2.0), Fe (0.1), Ca (2.0)	15	15.5
Mn (4.0), Ce (0.1), Co (2.0)[a]	10	10.2
V (0.05), Mg (1.0), Se (1.0)[a]	20	19.4
Cu (1.0), Zn (1.7), Al (0.14), Ni (0.038), Mn (0.035), W (0.03)[b]***	10	9.85
Al (0.004), Zn (0.003), Cu (0.130)***	15	15.8
Pb (0.09), Fe (0.009), Cu (0.18)***	20	21.0
Al (0.3), Mg (0.005), Cu (0.001), Pb (0.002)***	10	10.3
Zn (0.048), Pb (0.05), Cu (0.04)***	18	17.2
Cu (0.170), Co (0.01)***	15	15.7
Gun metal	4.9 %****	4.7 %

*Figure in bracket indicates the amount of metal ions in mg/10 mL; **Average of triplicate analysis; ***Corresponds to tungsten brass, aluminium tin bronze, ceco alloy, magnalium cast Z, kneiss metal, argental; ****Certified value; [a]In the presence of 30 mg ascorbic acid. [b]In presence of 0.5 mL of H_2O_2 [30 % w/v].

Conclusion

The Sn(II)-CHMPB complex, when extracted into dichloromethane after equilibration for 5-120 s from 0.02-0.05 M HCl medium containing 33 µg Sn(II) and 0.8-1.5 mL of 0.2 % (w/v) alcoholic solution of CHMPB in 10 mL aqueous phase, is highly stable (0.5 h) and can be safely used for the spectrophotometric determination of tin in trace amounts (optimum range- 0.22-3.16 ppm), giving satisfactory result in presence of a large number of elements and complexing agents in mg amounts. The method is simple, rapid, reliable and can be recommended for routine analysis of tin in a wide variety of samples. Detection limit of the method is 0.26 µg mL^{-1}. This is found to be better than most of the existing methods of microdetermination of tin using the spectrophotometric

TABLE-4
COMPARISON OF THE PROPOSED METHOD WITH THE EXISTING ONES

Aqueous conditions	Solvent (λ_{max}, nm)	Sandell's sensitivity, µg cm^{-2} (Molar absorptivity, L mol^{-1} cm^{-1})	Interfering metal ions	Ref.
Sn(II), Morpholine dithiocarbamate (MDTC), pH 5.0	Chloroform (360)	0.0169 (7.003×10^3)	–	[2]
Sn(II), 0.5-1.0 M H_2SO_4, thioglycolic acid, 5 % gumarabic sol. dithiol sol., colour development time 10 min	Chloroform (535)	0.0208 (5.8×10^3)	Bi(III), Hg(II), Ag(I), Cd(II), Cu(II), Mo(VI), W(VI)	[8]
Sn(II), 0.05-0.07 M HCl, 0.2 % 6-chloro-3-hydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran in acetone	Carbon tetrachloride (415)	0.0030 (3.92×10^4)	–	[9]
Sn(II), 0.05-0.55 M HCl, ascorbic acid, isoamylxanthate	Chloroform (350)	0.0130 (1.66×10^4)	Mo(VI), Ce(IV)	[10]
Sn(II), 1-[(2,3,4-trihydroxy benzene)azo]-4-benzoic acid (TKAB) nonionic surfactant OP, 0.2 M HCl	Chloroform (482)	0.0041 (2.86×10^4)	–	[11]
Sn(IV), pyrocatechol violet, Tween-20, cetyltrimethyl ammoniumbromide, pH 1.6-2.7 (with glycine buffer), N-(carboxymethyl)-N-(2-hydroxyethyl)-N,N'-ethylenediglycine, colour development time 30 min	Chloroform (660)	0.0012 (1.03×10^5)	Bi (III), Sb (V), Ti (IV), Mo (VI)	[12]
Sn(II), 0.02-0.05 M HCl, 0.2 % CHMPB in ethanol, 45-52 °C	Dichloromethane (417)	0.00244 (4.876×10^4)	34 metal ions do not interfere	Present method

technique because of its vast scope, lesser no. of interferences, rapidity and higher sensitivity (Table-4). The method proposed takes only 5 min for a single determination of Sn(II) in comparison to the existing methods. High selectivity of the method is evident from the non-interference of a large no. of elements, making it a more useful determination method compared with the existing methods.

ACKNOWLEDGEMENTS

The authors are thankful to Maharishi Markandeshwar University, Mullana and University Institute of Engineering and Technology, Kurukshetra University, Kurukshetra, India for providing laboratory facilities.

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