ferred to an Erlenmeyer flask containing an excess of potassium metaperiodate (50-100 mg) and 10 ml of ~$M/20$ borax solution. The contents of the flasks, except for arsenic(III), were boiled for 10-15 min and cooled to room temperature. $2M$ ammonium molybdate (10-15 ml) followed by 10 ml of chloroacetic acid buffer (pH 2·9) and potassium iodide (1 g) were then added and the iodine liberated was titrated with $0{\cdot}1N$ sodium thiosulphate. For As(III) boiling was not required. However, the reaction mixture was kept for 15 min at room temperature before the addition of ammonium molybdate solution. A blank of distilled water was taken through the whole process. The results are recorded in Table 1.

Estimation of bromide — A suitable aliquot of bromide was transferred to a titration flask containing an excess of potassium metaperiodate (50-70 mg) and 100 ml of $1N$ H_2SO_4. The reaction mixture was heated on a water-bath at 80-85° for 1 hr and air was constantly bubbled through the solution to expel bromine completely. The reaction mixture was cooled to room temperature, neutralized with 20 ml of $5N$ sodium carbonate solution and the iodate determined, as before, after masking periodate with molybdate. The results are recorded in Table 1.

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TABLE 1 — ESTIMATION OF BROMIDE, HYPOPHOSPHITE, PHOSPHITE, ARSENIC(III), SELENIUM(IV) AND TELLURIUM(IV)

Taken (mg)	Found (mg)	Taken (mg)	Found (mg)
BROMIDE		HYPOPHOSPHITE	
26·33	26·27	4·47	4·46
32·92	32·93	5·47	5·42
39·50	39·50	6·55	6·58
46·00	46·00	7·66	7·69
52·65	52·67	8·94	8·94
59·25	59·20	11·17	11·16
PHOSPHITE		ARSENIC(III)	
11·32	11·33	9·37	9·38
14·15	14·13	11·24	11·25
16·98	17·00	13·11	13·13
18·81	18·80	14·98	14·94
22·64	22·67	16·86	16·88
28·30	28·27	18·73	18·69
SELENIUM(IV)		TELLURIUM(IV)	
11·25	11·25	15·47	15·52
14·07	13·95	23·21	23·18
16·88	16·91	30·94	30·84
19·69	19·54	38·68	38·60
22·50	22·50	46·41	46·36
28·13	28·03	54·15	54·02

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Solvent Extraction of Gallium with Thiothenoyltrifluoroacetone: Direct Photometric Determination with Rhodamine B

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Thiothenoyltrifluoroacetone has been used for the solvent extraction of gallium. About 12·6 μg of gallium is quantitatively extracted at pH 6·5-7·5 with 10 ml of 0·001M STTA in benzene. Gallium is determined in the organic phase spectrophotometrically as a coloured complex with rhodamine B at 580 nm. The system obeys Beer's law in the concentration range 0·126-1·89 μg Ga(III)/ml. The complex is stable for 24 hr. The molar absorptivity is $3{\cdot}3\times10^4$ mol^{-1} cm^2 and sensitivity is 0·002 μg/cm^2. Gallium has been extracted and determined in a single extraction in the presence of many elements associated with it, such as indium, thallium and aluminium.

AMONGST β-diketones, acetylacetone[1-3] was used at pH 6-9 for the extraction of gallium. Not only the extraction was incomplete (97%), the process was time-consuming as it involved too many steps. The complexes of gallium, indium and aluminium with trifluoroacetylacetone[4] were separated by gas chromatography. Benzoylacetone and dibenzoylmethane[5] were used for the extraction of gallium at pH 4-5·5. The synergistic extraction of gallium with thenoyltrifluoroacetone (TTA) and tetraphenylarsonium chloride[6] was also reported, but this method suffered from several disadvantages, namely that the extraction was feasible at macrogram concentration, the pH of the extraction was very narrow and it was essential to use high reagent concentration. The extraction occurred only in the presence of the acetate ions.

A method for the solvent extraction of gallium with TTA was developed by us[7]. However, this method is not so sensitive in comparison to thiothenoyltrifluoroacetone (STTA) method, now being described in this paper, as the solvent system employed, viz. xylene, is not as efficient a solvent as benzene. It is observed that coloured species, $RHGaCl_4$, is more soluble in benzene than in xylene. Further $Ga(TTA)_3$ is not as easily dissociated as $Ga(STTA)_3$ for colour development with rhodamine B. The pH for complexation for TTA is 4·5 while for STTA it is 6·5.

The method proposed in this paper is advantageous, as it is possible to separate gallium from indium, thallium and aluminium, with which it is usually associated. The method is selective as it is possible to separate gallium from a large number of elements at trace concentrations.

Spectromom 204 spectrophotometer, digital pH meter (ECIL) and a wrist action flask shaker were used. Thiothenoyltrifluoroacetone (STTA) was synthesized by the procedure of Berg *et al.*[8]. A solution (0·001M) of STTA was prepared in benzene. A

0·5% solution of rhodamine B (BDH) was prepared in 6*M* HCl. A stock solution of Ga(III) was prepared by dissolving gallium nitrate octahydrate (0·36 g) in distilled water (100 ml) containing nitric acid (1%). The solution was standardized gravimetrically[9] and was found to contain 0·63 mg of gallium per ml. It was diluted to get the desired concentration.

General procedure — An aliquot of gallium nitrate solution containing 12·6 μg of gallium was taken and the *p*H adjusted to 6·5-7·5 with 0·01*M* nitric acid and 0·01*M* ammonia solution in a total volume of 25 ml. It was then shaken in a separatory funnel for 5 min with 10 ml of 0·01*M* STTA in benzene. The two layers were allowed to settle and separate. The aqueous phase was carefully withdrawn. The organic layer was once again shaken with 10 ml of 6*M* hydrochloric acid containing 1 ml of 0·5% rhodamine B[10] for 5 min. The two layers were allowed to settle and separate. The red-coloured complex was measured spectrophotometrically[10] at 580 nm against the reagent blank. The concentration of gallium (III) was computed from calibration curve.

Nature of complex species — In the extraction with β-diketone it is presumed that HSTTA combined with Ga(III) to form chelate at *p*H 6·5 in accordance with Eqs. (1) and (2).

$$HSTTA \rightleftharpoons H^+ + STTA^- \quad ...(1)$$

$$Ga^{3+} + 3(STTA^-) \rightarrow Ga(STTA)_3 \quad ...(2)$$

Now on equilibration of organic phase at 6*M* hydrochloric acid, the complex breaks to $GaCl_4^-$, which on association with RH^+ (R = rhodamine B, tetraethylrhodamine) gets extracted as ion associated complex. The mechanism of formation of ion-associated complex may be represented by Eqs. (3-5).

$$Ga(STTA)_3 \rightleftharpoons Ga^{3+} + 3STTA^- \quad ...(3)$$

$$Ga^{3+} + 4Cl^- \rightleftharpoons [GaCl_4]^- \quad ...(4)$$

$$RH^+ + GaCl_4^- \rightleftharpoons [RH^+ : GaCl_4^-]^\circ \quad ...(5)$$

Thus metals forming chloroanions with single charge give a 1:1 rhodamine B salt which is extractable. The other less important species of the dye are RH_2^{2+} and RH_3^{3+}, but in 6*M* HCl only RH^+ exists and the coloured species formed is $RHGaCl_4$ (ref. 11). Rhodamine B chlorogallate is soluble in water and usually extracted to different extent by different aromatic hydrocarbons like xylene and benzene.

Absorption spectra — The absorption spectrum of Ga(III)-rhodamine B complex in benzene containing STTA [Ga(III) = $1·8 \times 10^{-5}$*M*] showed strong absorbance at 580 nm. The absorption maxima for STTA is around 420 nm and it showed negligible absorbance beyond 520 nm. Thus the absorbance measured at 580 nm is exclusively due to $RHGaCl_4$ against the reagent blank. Hence all the measurements were, therefore, carried out at 580 nm. The colour of the complex is stable at least for 24 hr. Hence the absorbance was measured within 24 hr.

The molar absorptivity was $3·3 \times 10^4$ mol^{-1} cm^2 at 580 nm on the basis of gallium contents. The sensitivity of the method as defined by Sandell was 0·002 μg/cm^2.

Effect of pH — The extraction of gallium(III) in STTA-benzene was studied over the *p*H range 1-10. The extraction was 10·67% at *p*H 1 and increased to 95% at *p*H 6·0. The optimum *p*H for quantitative extraction of gallium was 6·5-7·5. The extraction decreased beyond *p*H 8·0. The $pH_{\frac{1}{2}}$ was 3·80.

The period of equilibration was varied from 1 to 20 min on a wrist action flask shaker. The extraction was quantitative after 5 min of equilibration.

Effect of salting-out agents — Ammonium, sodium, potassium, calcium and magnesium nitrates were tested as the salting-out agents in the concentration range 1-3*M*. It was observed that none of the salting-out agents enhanced the extraction of gallium.

Verification of Beer's law — Varying amounts of gallium(III) (1·126 μg-1·89 μg/ml) were extracted at *p*H 6·5 as per the general procedure. The absorbance was measured at 570, 580, 590 and 600 nm. It was observed that system obeyed Beer's law at *p*H 6·5-7·5 over the concentration range of 0·126-1·89 μg/ml of gallium at 580-590 nm.

Effect of varying reagent concentration — All factors being kept constant concentration and volume of the reagent were varied. The extraction was incomplete at [reagent] lower than 0·001*M*. There was no significant increase in the absorbance and hence in the extraction, when the concentration of reagent was increased from 0·001 to 0·002*M*. The use of varying volumes of 0·001*M* reagent showed that the extraction was quantitative with 10 ml of the reagent.

Effect of diverse ions — Several ions were examined for their effect on the extraction of gallium. The tolerance limit was set at the amount of foreign ion required to cause ± 2% error in the gallium recovery. The results recorded in Table 1 show that common inorganic anions and common organic complexing agents are tolerated in the ratio of 1:400. Most of the other ions are tolerated in the ratio of 1:40 and 1:20. The ions showing strong interference are

TABLE 1 — EFFECT OF DIVERSE IONS

[*p*H = 6·5; Ga(III) = 12·6 μg; and STTA-benzene = $1·0 \times 10^{-3}$*M*]

Tolerance limit 1×10^3 μg	Added ions
5·0	Sr^{2+}, Ba^{2+}, Rb^+, Cs^+, I^-, CN^-, SCN^-, $S^{2-}O_3^{2-}$, SO_2^{2-} SO_4^{2-}, PO_4^{3-}, CH_3COO^-, $C_2O_4^{2-}$, $Tart^{3-}$, $Malon^{2-}$, $Ascorb^-$
2·0	SeO_3^{2-}, TeO_3^{2-}
0·5	Hg^{2+}, Sb^{3+}, Pt^{4+}, Ir^{3+}, Rh^{3+}, Os^{3+}, Ru^{3+}, Al^{3+}, Ni^{2+}, Th^{4+}, Zr^{4+}, Be^{2+}, Ge^{4+}, ReO_4^-, F^-, Cit^{3+}
0·25	Ag^+, Pb^+, Tl^+, Cu^{2+}, Cd^{2+}, Au^{3+}, Pd^{2+}, Ti^{4+}, Fe^{3+}, Mn^{2+}, Sn^{2+}, In^{3+}, $Mo_7O_{34}^{6-}$ WO_4^{2-}, VO_3^-
None	Bi^{3+}, Zn^{2+}, U^{6+}, $EDTA^{4-}$

Interference eliminated by masking Sb(III), Rh(III), Ru(III) and Zr(IV) with tartaric acid, Mn(II) with oxalic acid. The interference due to Pd(II) was eliminated by extraction with dimethyl glyoxime and that due to Fe(III) by extraction with acetylacetone.

bismuth, zinc, cobalt, uranium(VI), EDTA and ascorbate. Several sequestering agents were used to eliminate the interference of some of the ions, e g. antimony(III), rhodium, ruthenium, zirconium and cerium(IV) were masked with tartaric acid whereas manganese was masked with oxalic acid. The interference due to palladium and iron(III) was eliminated by selective extraction[12] with dimethylglyoxime and acetylacetone respectively.

The method is rapid as extraction and determination required only 30 min. As little as 0·126 μg per ml of gallium can be determined. The results are reproducible. The average recovery of gallium is 99·8 ± 0·2%. The relative standard deviation is is ±1·12%.

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Use of Some Phenolic & Pyrazolone Derivatives as Acid–Base Indicators

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Nitro, nitroso, amino, hydroxylamino, hydroxy and carboxy derivatives of some phenols and 2-pyrazolin-5-ones have been prepared and their use as acid-base indicators studied. The pK_{In} values, pH range, and colour in acidic and alkaline media are reported for the indicators. It is found that the pK_{In} value for 1-phenyl-3-methyl-4-amino-2-pyrazolin-5-one tallies with that of methyl orange (3·7), and it has also comparable stability. Hence its use as a substitute for methyl orange is suggested.

WHILE preparing various phenolic and 2-pyrazolin-5-one derivatives in the course of our investigation on fungicides against blast disease of rice plant, we observed that some of these compounds behave as neutralization indicators. It is known[1] that phenolic derivatives like *p*-nitrophenol, cresol red, etc., act as indicators in acid-base titrations. According to chromophore theory, the presence of $-NO_2$, $-NH_2$, -NHOH and -OH groups enhances the sharp colour change from acidic to alkaline medium or vice versa. The present seventeen compounds, having both chromophore and auxochrome groups, satisfy all the requisites of ideal indicators[2].

2-Nitroso-, 2-carboxy- and 2-nitro-resorcinols, 2-nitro-1-naphthol, 2-nitro-1-naphthol-3-carboxylic acid, 3-nitro-1-naphthol-2-carboxylic acid, 1-nitro-2-naphthol, 1-nitro-2-naphthol-3-carboxylic acid and 3-nitro-2-naphthol-1-carboxylic acid (Sr No. 1-9, Table 1) were prepared by standard methods[3-5]. 1-(2,4-Dinitrophenyl)-3-methyl-2-pyrazolin-5-one (Sl No. 16, Table 1) was also prepared by a reported procedure[6].

For the preparation of 6-nitro-*o*-cresol, 3-nitro-*p*-cresol and 6-nitro-*m*-cresol (Sl No. 10-12, Table 1), each of the compounds, *o*-cresol, *p*-cresol and *m*-cresol (2 g) was dissolved separately in pyridene (20 ml) and conc. HNO_3 (10 ml) added dropwise until effervescence stopped. The contents were cooled for 1 hr and ice-water (20 ml) was added. The separated compounds were filtered, recrystallized from ethanol; m.p. 69·5° (Sl No. 10), 77° (Sl No. 11), 56° (Sl No. 12); yield 65-75%.

For the preparation of 1-phenyl-3-methyl-, 1-acetamido-3-methyl- and 3-methyl-4-hydroxy-amino-2-pyrazolin-5-ones (Sr No. 13-15, Table 1), the three different 4-nitroso-2-pyrazolin-5-ones[7] (1 g each) were dissolved separately in the minimum amount of absolute ethanol and zinc (1 g) and calcium chloride solution (10 ml) were added. The mixtures were then refluxed over a water-bath for 1 hr, or until there was a marked colour change in the solution. The reaction mixture was filtered hot and excess of ethanol evaporated off. It was then allowed to cool (kept overnight) when crystals separated. The compounds were filtered, recrystallized, analysed for C, H and N. The analytical data are given in Table 2.

For the preparation of 1-phenyl-3-methyl-4-amino-2-pyrazolin-5-one (Sl No. 17, Table 1), 1-phenyl-3-methyl-2-pyrazolin-5-one[3] (1 g) was dissolved in the minimum amount of sodium hydroxide solution (10%). The solution was heated over a low flame while stirring it continuously. Solid sodium dithionite was added in small portions until the yellow colour of the solution changed to orange-red. The reaction mixture was kept overnight, when dark red crystals separated. The compound was filtered, recrystallized from ethanol, m.p. 186°, yield 70%. The same compound was also obtained, by carrying out the reduction in zinc and acetic acid medium (Found: C, 63·39; H, 5·81; N, 22·12. $C_{10}H_{11}N_3O$ requires C, 63·49; H, 5·82; N, 22·22%).

Preparation of the indicator solutions — 0·05 g of the indicator sample was dissolved in the minimum volume of ethanol at room temperature and volume made up to 100 ml by the addition of distilled water. In some cases, a slight precipitate was formed at this stage, which was filtered off.

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