

prepared by standard methods described in the literature. The purity was checked by TLC. The experimental procedure followed for the kinetic study was essentially that of Singh and Peacock<sup>13</sup>, and Reinlander<sup>14</sup>. The spectra were recorded on a Bruker WM-300 instrument at 75 MHz in CDCl<sub>3</sub> and referenced to TMS.

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## ISONITROSOTHIOCAMPHOR AS A SPECTROPHOTOMETRIC REAGENT FOR PLATINUM

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THE use of isonitrosothiocamphor (INTC) as an analytical reagent for palladium<sup>1</sup>, cobalt<sup>2</sup> and copper<sup>3</sup> has been described earlier. At room temperature platinum (IV) shows no visible colour reaction with INTC, but forms a greenish chelate while heating on a water bath. The chelate is extractable into chloroform. A method has therefore been devised to determine platinum (IV) spectrophotometrically.

Isonitrosothiocamphor (INTC) was prepared by the reported method<sup>4</sup> and a solution of the reagent in ethanol (0.4%, w/v) was used. One gram of chloroplatinic acid (Johnson and Matthey) was dissolved in distilled water (100 ml) and was standardized<sup>5</sup>. Sample solutions of platinum were prepared by dilution of the stock solution.

Chloroform (E. Merck) was distilled before use. All other reagents used were of analytical grade. Stock solutions of the desired ions were prepared from the corresponding salts and the metal contents determined by conventional methods<sup>5</sup>. Potassium hydrogen phthalate sodium hydroxide buffer (pH 7-8) was used to adjust the pH of aqueous solutions. Absorbance and pH measurements were made as reported earlier<sup>1</sup>.

To an aliquot of the sample solution of platinum (IV) (100-200 µg) was added ethanolic solution of INTC (0.5 ml of 0.4%), followed by addition of the buffer solution. The volume of the aqueous phase was maintained at 10 ml throughout the work. The mixture thus prepared was then heated (10 min) on a boiling water bath, cooled to room temperature, and then equilibrated (1 min) with chloroform (10 ml). The separated organic layer was poured over anhydrous sodium sulphate to remove any residual water. Finally the absorbance of the chloroform extract at 369 nm was measured against reagent blank. Platinum (IV) was determined from the calibration curve. To test for interference due to other ions, the ion was added to the system before addition of the reagent.

The extraction of platinum complex was investigated in the pH range 0-10. However, the chloroform extracts showed maximum and steady

absorbance (for at least 24 h) when the extractions were carried out at pH in the range 6–9. The extraction of the aqueous phase was repeated till an organic extract that showed virtually no absorbance was obtained, which indicated complete and quantitative recovery of platinum from the aqueous phase.

The absorption spectrum of the Pt(IV)–INTC complex in chloroform shows absorption maxima at 369 and 435 nm. The reagent blank shows insignificant absorbances from 340 nm onwards. Hence the wavelength of 369 nm was selected for analytical measurements for higher absorbance.

It was noted that 0.5 ml of 0.4% ethanolic solution of INTC was the optimum reagent concentration to extract 100–200  $\mu\text{g}$  of Pt(IV) in a single extraction. Higher reagent concentration was avoided, since in the presence of a higher concentration of INTC the absorption of the blank is high. Beer's law was obeyed over the concentration range 2–25 ppm of platinum (IV). The molar absorptivity and sensitivity index (on the basis of Pt content) of the colour system were found to be  $0.82 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.023 \mu\text{g Pt/cm}^2$  respectively.

The precision and accuracy of the method were tested by analysing solutions containing a known amount of platinum. The average of six determinations (190  $\mu\text{g}$  Pt) was found to be 191.33  $\mu\text{g}$ , with a relative mean deviation of 1.91%.

A deviation of not more than  $\pm 3\%$  from the recovery of platinum was taken as the standard tolerance limit in testing for interference due to other ions. In the estimation of 190  $\mu\text{g}$  of Pt, the following ions did not interfere when present in the amounts (mg) shown in parentheses: Cd(II) (4.5), Ca(II) (5.2), Ce(III) (4), Cr(III) (4.5), Pb(II) (5.5), Mn(II) (3.2), Th(IV) (3), U(VI) (4), Zn(II) (5.5), Zr(IV) (4.5), Bi(III) (3), La(III) (4.5), Mg(II) (1), Al(III) (1), Mo(VI) (4.5), Palladium(II) (0.5), Cu(II) (0.5). These ions could be tolerated in the presence of thiosulphate and tartrate respectively. Interference due to Ni(II) (0.5) and Co(II) (0.5) was avoided by using EDTA as the masking agent. In the presence of silver(I), platinum(IV) developed no colour with INTC. High results are obtained in presence of rhodium(III).

Among the anions tested, 10 mg each of thiocyanate, thiosulphate, iodide, EDTA, citrate, tartrate, oxalate and phosphate did not interfere. Less than 0.5 mg of fluoride could be tolerated. Ascorbate and thiourea interfered.

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## CHEMICAL ANALYSIS OF *CALOTROPIS PROCERA* LATEX

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HESSE and his collaborators<sup>1</sup> detected, rather interestingly,  $\alpha$ -lactuceryl as the only constituent in the ethanolic extract of *Calotropis procera* latex. The latex also revealed the presence of a variety of cardioactive poisons, terpenoid alcohols, esters involving steam-volatile and other long-chain fatty acids<sup>2,3</sup>, taraxasterol, calotropagenin and six of its glycosides<sup>4–11</sup>, and three additional compounds<sup>12</sup>. All these glycosides contained a common aglycone<sup>5</sup> to which a structure<sup>13–15</sup> was assigned and subsequently established by its partial synthesis<sup>16,17</sup>. Table 1 lists the compounds hitherto identified and isolated in pure form from *Calotropis procera* latex, leaves and stem, with their molecular formulae and melting points, and the available relevant references.

Thin-layer chromatography of *Calotropis procera* latex extract revealed more than 22 spots on exposure of the plate to iodine vapour and sulphuric acid spray (60% v/v) and subsequent heating to 105°C for 5 min. This observation prompted the authors to make a systematic analysis of the latex and look for compounds yet undetected and/or unidentified.

*Calotropis procera* latex was collected as described earlier<sup>18</sup>. The dried solid was extracted exhaustively with ethanol and the pooled concentrate on filtration deposited white shining needles melting at 224–225°C. The pentacyclic triterpenol answered to the formula  $\text{C}_{30}\text{H}_{50}\text{O}$  deduced from its elemental analysis and molecular weight read from its mass spectrum. The properties and melting point of the