

Selective Microdetermination of Uranium Using Weisz Ring Oven Technique: Application to an Indirect Determination of Trace Amounts of Arsenic in Tobacco

A. C. HANDA

Department of Chemistry, Hindu College, Maurice Nagar, Delhi 110007

and

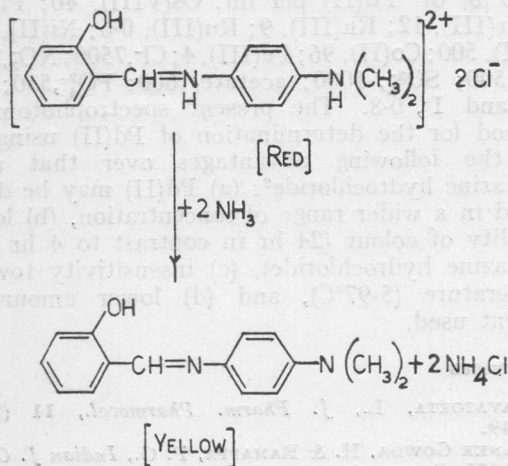
K. N. JOHRI

Department of Chemistry, University of Delhi, Delhi 110007

Received 31 August 1974; accepted 20 May 1975

A procedure for the microdetermination of uranyl ions in the presence of a large number of adverse ions has been described involving the use of the Weisz ring oven. The chromogenic reagent that has been employed is the schiff base of N,N-dimethyl-*p*-phenylenediamine and salicylaldehyde which, under the specified conditions, gives a red-coloured product with uranyl ions. The visual identification range has been found to be 0.07-1.5 µg of uranyl ions present in the 22 mm diameter ring. The present procedure for uranyl ions has also been extended to the trace amount determination of arsenic in tobacco.

It has been observed that N,N-dimethyl-*p*-phenylenediamine salts give red coloured protonated¹ schiff bases with aromatic aldehydes like salicylaldehyde. This red compound when treated with ammonia turns yellow due to the formation of non-protonated form.



The yellow compound when treated with uranyl ions produce a red-coloured product² the intensity of which depends directly on the amount of uranyl ions. This reaction has been utilized in the present studies for a highly selective microdetermination of uranyl ions employing ring oven technique³⁻⁶ along with an indirect determination of trace amounts of arsenic in tobacco.

A Weisz ring oven (National Appliance Co., Portland, Oregon, USA) with a suitable power unit yielding 25 V from 220 V/50 cycles ac mains, was

used. A microsyringe (Hamilton Co. Inc., Whittier, California, USA) of minimum 1 µl capacity for the application of test solutions was employed. Filter paper circles (Whatman No. 41, 55 mm diam. were washed free from iron with 0.1M HCl on the ring oven and then thoroughly washed with doubly distilled water, dried and used.

Uranyl nitrate and sodium arsenate solutions were prepared in water containing a few drops of dil. AcOH. Doubly distilled and deionized water and AR grade reagents were used throughout.

Preparation of the reagent — In a test tube, 10 ml aq. 1% solution of N,N-dimethyl-*p*-phenylenediamine dihydrochloride (E. Merck) was mixed with 1 ml ethanolic 10% solution of salicylaldehyde and immersed the test tube for a few min in a boiling water-bath. The contents of the tube were cooled and added just sufficient amount of ammonia solution (1:5) when the blood-red solution changed to yellowish brown (addition of ammonia must be done just before the experiment).

Determination of U(VI) ions — A circle of Whatman No. 41 filter paper was placed on the ring oven set at 100-110°C and a known amount of uranyl ions transferred to the centre of the filter paper by means of a micro-syringe and the paper dried. Next, a drop of aq. sodium arsenate solution (5%) was applied followed by one drop of aq. ammonium acetate (10%) and a drop of dil. AcOH. The paper was dried when all the uranyl ions were fixed as uranyl ammonium arsenate. The paper was removed from the oven and washed thoroughly on a suction pad first with luke warm water and then with cold water. The paper was carefully removed from the suction pad and placed again on the ring oven. The fixed uranyl ions were washed into the ring zone with 0.01M HCl, the paper dried and sprayed with the reagent, and dried at room temperature. A sharp red ring against a yellow background indicated the presence of uranyl ions. After 10 min the intensity of the red ring was compared visually with the red rings comprising the standard scale prepared by taking 1, 3, 5, 7, 9, 11, 13 and 15 µl of the standard U(VI) solution (0.1 mg/ml) and the amount in the unknown ring computed.

The visual identification range of the proposed method was found to be 0.07 to 1.5 µg of uranyl ions when the ring diameter was 22 mm. Outside this range visual comparison was difficult. Results of some typical experiments are given in Table 1.

Determination of arsenic in tobacco — NaOH (3 g) was fused in a 100 ml nickel crucible, cooled and

TABLE 1 — DETERMINATION OF UO₂(II)

UO ₂ (II) (mg/ml)		Error (%)
Taken	Found	
0.45	0.46	+2.2
0.10	0.10	0.0
0.35	0.33	-5.7
0.65	0.62	-4.6
0.90	0.93	+3.3

TABLE 2 — DETERMINATION OF ARSENIC IN TOBACCO

Sample No.	Amount of tobacco taken (g)	Amount of arsenic taken (μg)	Amount of arsenic found (μg)	Error (%)
—	—	10	10.3	+3.0
—	—	15	15.4	+2.7
—	—	20	20.7	+3.5
—	—	50	49.1	-1.8
A	5	—	4.5	—
B	7	—	6.3	—
C	9	—	3.5	—
D	6	—	5.8	—
E	10	—	4.7	—

tobacco sample (1 g) and Na_2O_2 (1.5 g) were added on to the solidified mass. It was heated gently for 10 min while adding Na_2O_2 (2×1 g) intermittently until there was a complete decomposition of the organic matter.

The above procedure was repeated with more of tobacco and Na_2O_2 till 5 g of tobacco sample had been decomposed. The crucible was finally heated for 15 min, cooled and water (15 ml) added. The contents of the crucible were warmed on a steam-bath until the melt was completely disintegrated. The solution was centrifuged and the residue washed with water. The centrifugate and washings were collected in a 100 ml conical flask, acidified with HCl (6M) and boiled gently to decompose peroxide. The solution was cooled and conc. HCl (15 ml) added followed by aq. KI (2 ml, 15%) and SnCl_2 solution (1 ml, 40%) in conc. HCl. The contents were kept for 30 min at room temperature. Zinc metal (3.4 g) was added and the evolved arsine (AsH_3) decomposed to metallic arsenic by heating the tube. Metallic arsenic was dissolved in a minimum amount of hot HNO_3 and the resultant solution neutralized with dil. NaOH. It was reacidified with AcOH (2N) and the final volume made up to 2 ml by evaporation and dilution. An aliquot of the solution was subjected to the ring oven method as described above whereby the arsenic content of tobacco was determined and the results are given in Table 2. The efficacy of the above alkaline peroxide fusion method was checked separately by ring-colorimetric and volumetric (potassium bromate)⁸ methods. In both the methods known amounts of arsenic as arsenic trioxide were taken. A few representative ring colorimetric results have also been incorporated in Table 2.

Uranium forms a red insoluble chelate with the reagent under the specified conditions. The interference of various foreign ions was studied by developing rings for $\text{UO}_2(\text{II})$ ions with and without the foreign ions taken in varying amounts up to 25 μg . The ions which did not interfere in the procedure are: NH_4^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ag^+ , $\text{Cu}(\text{II})$, $\text{Hg}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Sn}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Bi}(\text{II})$, $\text{Be}(\text{II})$, $\text{Mg}(\text{II})$, $\text{Ca}(\text{II})$, $\text{Ba}(\text{II})$, $\text{Sr}(\text{II})$, $\text{Al}(\text{III})$, $\text{Mn}(\text{II})$, $\text{Cr}(\text{III})$, $\text{As}(\text{III})$, $\text{Sb}(\text{III}, \text{V})$, $\text{Ni}(\text{II})$, $\text{Co}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Ga}(\text{III})$, $\text{In}(\text{III})$, $\text{Tl}(\text{I})$, $\text{Se}(\text{IV}, \text{VI})$, $\text{V}(\text{V})$, $\text{Au}(\text{III})$, $\text{Pt}(\text{IV})$, $\text{Pd}(\text{II})$, $\text{Ru}(\text{III})$, $\text{Rh}(\text{III})$, $\text{Os}(\text{VIII})$, $\text{Ir}(\text{IV})$, $\text{La}(\text{III})$, $\text{Nd}(\text{III})$, $\text{Pr}(\text{III})$, $\text{Gd}(\text{III})$, $\text{Sm}(\text{III})$, $\text{Y}(\text{III})$,

$\text{Hf}(\text{IV})$, $\text{Zr}(\text{IV})$, $\text{Re}(\text{VII})$, $\text{W}(\text{VI})$, NO_2^- , NO_3^- , CO_3^{2-} , Cl^- , Br^- , I^- , SCN^- , SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_8^{2-}$, $\text{S}_2\text{O}_8^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, ClO_3^- , ClO_4^- , BrO_3^- , IO_3^- , $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$. $\text{Th}(\text{IV})$, $\text{Ce}(\text{III}, \text{IV})$, $\text{V}(\text{IV})$, $\text{Fe}(\text{II}, \text{III})$, S^{2-} and PO_4^{3-} ions, however, interfere.

The serious interference caused by fluoride, oxalate, citrate, tartrate, and EDTA is obviated by boiling the test sample three to four times with HNO_3 to almost dryness followed by evaporation with water. Interference due to fluoride and EDTA has also been overcome by treating the sample solution with a mixture of aluminium and nickel ions in the presence of ammonium acetate and AcOH. During this operation aluminium ions form more stable complex with fluoride ions than uranium ions whereas nickel ions mask EDTA. The high selectivity of the determination of uranyl ions has been achieved by incorporating arsenate ions as the fixing agent for uranyl ions under the specified conditions.

During the determination of arsenic in tobacco, alkaline peroxide method has been preferred over the conventional wet acid digestion process. Since the organic materials (pyridine and other nitrogen ring compounds) present in tobacco are hard to decompose, wet oxidation takes very long time with a large consumption of acids. This difficulty has been obviated in the present alkaline peroxide method for the decomposition of organic matter. The method has been found highly suitable in the case of tobacco.

Acknowledgements are due to Messrs India Tobacco Company for supplying the tobacco samples.

References

- GOLDSTEIN, G. & STARK, C., *Anal. chim. Acta*, **19** (1958), 439.
- JUNGREIS, E. & LINABEN-DOR, *Anal. chim. Acta*, **30** (1964), 405.
- JOHRI, K. N., HANDA, A. C. & MEHRA, H. C., *Anal. chim. Acta*, **57** (1971), 217.
- HANDA, A. C. & JOHRI, K. N., *Res. Ind.*, **16** (1971), 292.
- HANDA, A. C. & JOHRI, K. N., *Anal. chim. Acta*, **59** (1972), 156.
- WEISZ, H., *Microanalysis by the ring oven technique* (Pergamon Press, London), 1970.
- BELCHER, R., NUTTEN, A. J. & MACDONALD, A. M. G., *Quantitative inorganic chemistry* (Butterworths, London), 1970, 251.

5-Hydroxy-1,4-naphthaquinone (Juglone), a New Indicator in Acidimetry & Alkalimetry

S. S. SAWHNEY & NARESH C. TREHAN

Department of Chemistry, D.A.V. (Postgraduate) College Dehra Dun

Received 6 January 1975; accepted 6 May 1975

5-Hydroxy-1,4-naphthaquinone has been successfully used in acidimetry and alkalimetry. With juglone the pH range for colour change (yellow \rightarrow violet) is 7.8-9.9, thereby rendering it more suitable for acid-base titrations as compared to phenolphthalein.

NAPHTHAQUINONE and its derivatives have been used in industry¹, medicine² and for qualitative and quantitative estimation of metal