

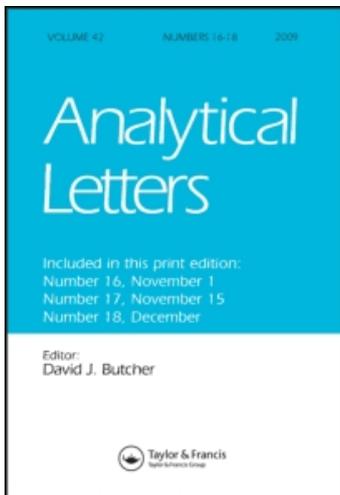
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**XYLENOL ORANGE AS A NEW REAGENT FOR THE
COLORIMETRIC DETERMINATION OF SELENIUM AND
TELLURIUM**

Key Words: Xylenol orange, colorimetric determination, selenium and tellurium.

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Summary

Xylenol orange is proposed as new sensitive reagent for the colorimetric determination of selenium and tellurium. The reagent forms a pink colored radical cation with selenite and tellurite instantaneously at room temperature in slightly acidic medium. The pink species exhibits an absorption maximum at 568 and 569 nm with a molar absorption coefficient of 2.69×10^4 and 2.82×10^4 l mol⁻¹ cm⁻¹ and Sandell sensitivity of 2.94 and 4.52 ng cm⁻² for selenite and tellurite, respectively. A 10-fold molar excess of the reagent is necessary for the development of the maximum color intensity. Beer's law is obeyed over the concentration range 0.10-5.50 and 0.13-6.38 µg ml⁻¹ of selenium and tellurium, respectively with an optimum concentration range of 0.35-5.10 and 0.40-6.00 µg ml⁻¹, respectively using Ringbom method. The effects of acidity, time, temperature, order of addition of reagent, reagent concentration and the tolerance

limit of the method towards various cations and anions usually associated with selenium and tellurium are reported. The proposed method is extremely sensitive, reproducible and has been satisfactorily applied to the determination of trace amount of selenium in polluted water, plant material and medicated shampoo.

Introduction

Selenium is a naturally occurring trace element recognized for its unique properties intermediate between metals and non-metals. Selenium is widely distributed in nature in relatively small concentrations in rocks, plants, coal and other fossil fuels. Volcanic eruption, smelting ceramics and metallurgical operations, manufacture of insecticides, glass and electronic goods are also major sources of selenium in the environment¹. Selenium enters into natural waters through seepage from seleniferous soils and industrial waste². Selenium liberated into the environment accumulates in soil and undergoes complex biogeochemical reaction leading to organoselenium compounds, which are much more toxic than inorganic selenium compounds. Because of its significance, several methods based on different analytical techniques have been reported for the determination of selenium³⁻¹¹.

Several methods including either classical or instrumental analysis were applied for the determination of tellurium. Using gravimetric analysis, phenylhydrazinesulphonic acid¹² and morpholine-4-carbodithioate¹³ were used for tellurium determination. Egikyan and Gaibakyan applied paper chromatography¹⁴ for separation and determination of tellurium in acidic medium. Dindi and Reddy¹⁵ determined tellurium simply by addition of a known excess of ammonium cerium (IV) sulphate and titrating excess cerium against ferrous ion (II). Tellurium in its alloys was analysed by back titration of the excess $K_2Cr_2O_7$ against Fe (II) using N-phenylanthranilic acid¹⁶. Hassan¹⁷ determined tellurium in simple solution or binary mixture by polarographic

analysis. Amperometric titration with the use of either methylthymol blue¹⁸ or permanganate¹⁹ reagents was found to be suitable for tellurium determination. Photometric titration of Te (IV) against $K_2Cr_2O_7$ at 380-430 nm was investigated²⁰. Atomic absorption spectrometry was used for evaluating Te (IV) in urine by hydride generation technique²¹.

Xylenol orange (XO) is well known as a low selective reagent used in complexometric²², photometric titrations^{23,24} and in spectrophotometric determination²⁵ of rare earth elements. The reaction of XO with Zr (IV) depends on the formation of radical cation²⁶. The sensitivity of the reaction with XO can be substantially enhanced in the presence of cationic surfactants indicating the formation of radical cation²⁷⁻²⁹. However, the need for a highly sensitive continuous method of selenium and tellurium determinations using XO has not yet been satisfied.

The aim of the present work is to use XO for the rapid determination of selenium and tellurium. The proposed method offers the advantages of simplicity, rapidity, high sensitivity and the determination of selenium and tellurium without the need for extraction or heating. The proposed method is suitable for the determination of trace amount of selenium in environmental samples and offers several advantages over reported methods.

Experimental

Reagents and Solutions

All of the used chemicals were of analytical grade. Reagents and the solutions were made with a doubly distilled water. Sodium selenite and sodium tellurite were obtained from BDH chemical company. 10^{-3} M solutions were prepared by dissolving their appropriate weights in water. The stock solution was further diluted as needed.

A 10^{-3} M xylenol orange (Fluka, Switzerland) was prepared by dissolving the accurate weight in water. The absence of metal traces in XO reagent was proved by comparison of the spectra of XO solutions containing 0.1 M EDTA with those without EDTA, both of pH 4 up to 8.

Instrumentation

A Perkin-Elmer Lambda 3B spectrophotometer with matched 10 mm silica cells was used for all spectral and absorbance measurements. The pH of solutions was checked using an Orion Model 601 A/digital Ionalyzer.

Procedure

Transfer an aliquot of the stock solution containing 2.5-137.5 and 3.25-159.5 μg of selenium (IV) and tellurium (IV) solution, respectively into a series of 25 ml calibrated flasks. Add 5 ml of universal buffer solution of pH 6.59 and 2 ml of 10^{-3} M XO solution to each flask and dilute to the mark with doubly distilled water. Mix well and measure the absorbance at 568 and 569 nm for Se(IV) and Te(IV), respectively against the corresponding reagent blank prepared in the same manner. The graph of absorbance versus concentration of Se (IV) or Te(IV) is a straight line passing through the origin.

Procedure for the determination of selenium in polluted water.

To an aliquot of (\sim 200-250 ml) of test solution, 10 ml of mixture containing 1 : 1 perchloric acid and aqua-regia was added, then evaporated to dryness. The residue was extracted in dilute HCl. The pH of the extracted solution was adjusted to 9.75 by adding 0.1 M NaOH to achieve the same pH as for sodium selenite. Analyse 5 ml of this solution for selenium as recommended above.

Procedure for selenium in plant material

Take 5 g of plant material in a 100 ml roundbottom flask, add 10 ml nitric acid and heat for 20 min., then add 0.5 ml perchloric acid and heat for another 10 min or until the evolution of fumes of perchloric acid, whichever is earlier. Add 5 ml of HCl and heat for 10 min, then adjust the pH to 9.75 with 0.1 M NaOH to achieve the same as for sodium selenite. Dilute the contents to 50 ml after adding 10 ml of 0.05 M EDTA solution and then follow the above recommended procedure.

Procedure for selenium in medicated shampoo.

Transfer 1 ml of medicated shampoo into a 100 ml beaker, add 5 ml mixture of 1 : 1 perchloric and nitric acid and evaporate to dryness. Extract the residue in dilute HCl and adjust the pH to 9.75 by adding 0.1 M NaOH in distilled water. A 100 ml stock solution was prepared from which an aliquot was taken and subjected to the recommended procedure.

Results and Discussion

Selenite and tellurite in slightly acidic medium formed a pink color with a yellow XO depending on the formation of radical cation. The absorption spectra of the reaction product showed characteristic maxima at 568 and 569 nm for Se(IV) and Te(IV), respectively at pH 6.59, while that of XO has an absorption maximum at 424 nm at the same pH value [Fig. 1]. The intensity of pink color of XO radical increases as the concentration of Se (IV) or Te (IV) increase.

Effect of variables

Since the color development is acidity dependent, the variation of pH was studied. It was found that the maximum absorbance was obtained, on using buffer solution of pH 6.59 [Fig.2], since the results are highly concordant at this pH

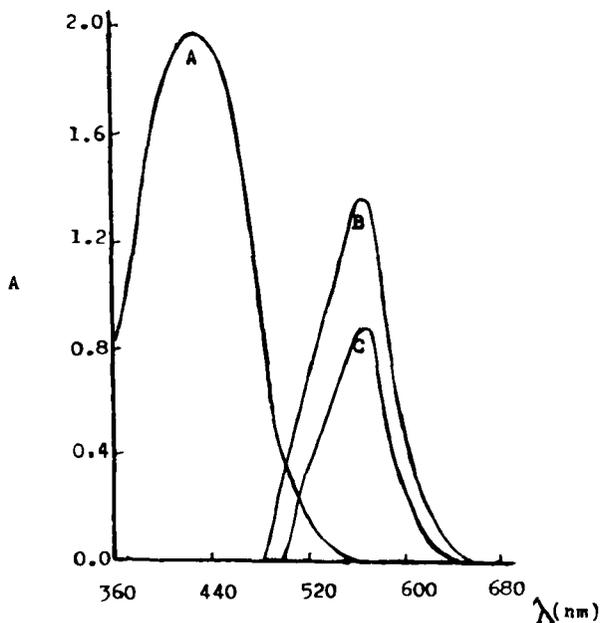


Fig. (1) : Absorption spectra of A) 8×10^{-5} M XO with pH 6.59, B) and C) is 4 $\mu\text{g/ml}$ Se (IV) and Te (IV) with 8×10^{-5} M XO using A) as a blank

value. The amount of pH 6.59 buffer added to 25 ml of solution was also investigated and it was found that 15 ml gave marginally the highest absorbance value.

At room temperature (25 ± 2 °C), the maximum absorbance is obtained instantaneously after mixing the components, and stable for a week at least. Raising the temperature up to 65°C has no effect on the color formation. The order of mixing of reagents seriously affects the absorbance value, however, addition in the order buffer-XO- Se (IV) or Te (IV) gives the best results.

When various concentration of XO was added to a fixed concentration of Se (IV) or Te(IV), 2 ml of 10^{-3} M solution was found to be sufficient for production

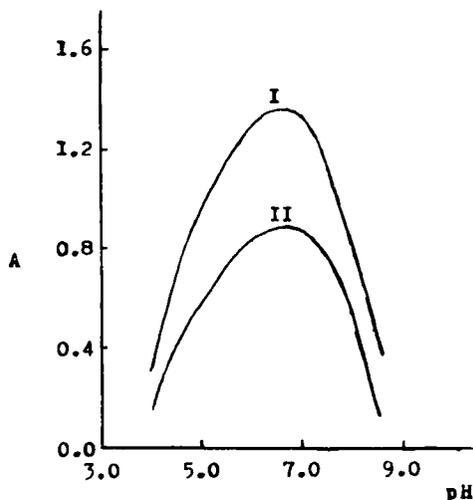


Fig. (2) : Effect of different pH on the absorbance of I-Se(IV) and II-Te(IV) using XO.

of maximum and reproducible color intensity. Higher concentrations of the reagent did not affect the color intensity [Fig. 3].

Quantification

A linear correlation was found between absorbance and concentration in the ranges 0.1-5.5 and 0.13-6.38 $\mu\text{g ml}^{-1}$ of Se (IV) and Te (IV), respectively. For more accurate analysis, Ringbom optimum concentration range was found to be 0.25-5.10 and 0.4-6.0 $\mu\text{g ml}^{-1}$, for Se(IV) and Te (IV), respectively. The correlation coefficients, intercepts and slopes for the calibration data for Se (IV) and Te (IV) are calculated using the least-squares method (Table1).

The reproducibility of the procedure was determined by running ten replicate samples, each containing 4 $\mu\text{g ml}^{-1}$ of Se (IV) or Te (IV) in the final

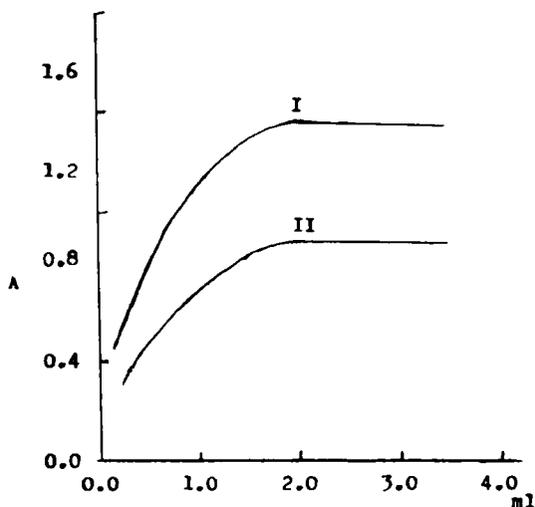


Fig. (3) : Effect of XO concentration on $4.0 \mu\text{g ml}^{-1}$ of I-Se(IV) and II- Te (IV).

assay solution. At this concentration, the relative standard deviation was 0.72 and 0.98% for Se (IV) and Te (IV), respectively.

The molar absorptivities (ϵ) and Sandell sensitivities were calculated and found to be 2.69×10^4 and $2.82 \times 10^4 \text{ l.mol}^{-1} \text{ cm}^{-1}$ and 2.94 and 4.52 ng cm^{-2} , for Se (IV) and Te (IV), respectively. In order to determine the accuracy and precision of the method, solution containing six different concentrations of Se (IV) or Te (IV) were prepared and analysed in quantuplicate. The measured standard deviation (s), relative standard deviation (S_r), the standard analytical errors and confidence limits (Table 2) can be considered satisfactory, at least for the levels of concentrations examined.

The influence of 38 kinds of ions on the determination was examined. The ions tested were added individually to a solution containing $4 \mu\text{g ml}^{-1}$ of Se (IV) or Te (IV). A maximum error of 2% in the absorbance reading was considered

Table (1): Quantitative parameters for the determination of Se (IV) and Te (IV) using XO.

| Parameter | Se (IV) | Te (IV) |
|--|--------------------|--------------------|
| pH | 6.59 | 6.59 |
| λ_{\max} | 568 | 569 |
| Beer's law limits / $\mu\text{g ml}^{-1}$ | 0.10-5.50 | 0.13-6.38 |
| Ringbom conc. Range / $\mu\text{g ml}^{-1}$ | 0.35-5.10 | 0.40-6.00 |
| Molar absorptivity, $\text{l. mol}^{-1}\text{cm}^{-1}$ | 2.69×10^4 | 2.82×10^4 |
| Sandell sensitivity, ng cm^{-2} | 2.94 | 4.52 |
| Range of error, % | ± 1.5 | ± 1.6 |
| Regression equation ^a | | |
| Intercept | 0.02 | -0.011 |
| Slope | 0.34 | 0.22 |
| Correlation coefficient | 0.9996 | 0.9988 |
| Standard deviation % | 0.72 | 0.98 |

$$A = a + bc \quad \text{where } c \text{ is the concentration in } \mu\text{g ml}^{-1}.$$

tolerable. The tolerance limit of foreign ions is given in Table (3). Thus, the data in this Table indicate the reasonable selectivity of the method in the presence of associated ions.

Analytical Application :

In order to confirm the usefulness of the proposed spectrophotometric method, it has been applied to the determination of Se(IV) in natural and polluted water, plant material and medicated shampoo (Table 4). Results of analysis of

Table (2) : Evaluation of accuracy and precision of the proposed colorimetric method.

| Ions | Taken $\mu\text{g ml}^{-1}$ | Found ^a $\mu\text{g ml}^{-1}$ | S | S _r % | Standard error | Confidence limits |
|---------|--------------------------------|---|------|------------------|-------------------|----------------------|
| Se (IV) | 0.9 | 0.892 | 0.04 | 0.63 | 0.016 | 0.892 ± 0.050 |
| | 1.8 | 1.810 | 0.06 | 0.71 | 0.024 | 1.810 ± 0.070 |
| | 2.7 | 2.717 | 0.09 | 0.75 | 0.037 | 2.717 ± 0.110 |
| | 3.6 | 3.560 | 0.05 | 0.61 | 0.020 | 2.560 ± 0.060 |
| | 4.5 | 4.550 | 0.10 | 0.84 | 0.041 | 4.550 ± 0.125 |
| | 5.4 | 5.330 | 0.08 | 0.79 | 0.033 | 5.330 ± 0.095 |
| | Mean | | | 0.72 | 0.029 | |
| Te (IV) | 1.0 | 1.016 | 0.03 | 0.78 | 0.012 | 1.016 ± 0.035 |
| | 2.0 | 1.98 | 0.07 | 0.99 | 0.029 | 1.98 ± 0.080 |
| | 3.0 | 2.96 | 0.11 | 1.28 | 0.046 | 2.96 ± 0.140 |
| | 4.0 | 4.06 | 0.09 | 0.98 | 0.037 | 4.06 ± 0.110 |
| | 5.0 | 4.92 | 0.05 | 0.78 | 0.020 | 4.92 ± 0.060 |
| | 6.0 | 6.09 | 0.10 | 1.17 | 0.041 | 6.09 ± 0.125 |
| | Mean | | | 0.98 | 0.031 | |

a Average of six determinations.

these samples showed a good correlation with those obtained applying the 3,3'-diaminobenzidine method³⁰. The performance of the proposed method was judged through calculation of student's t- and F-values, at 95% confidence limit, and the results showed that the calculated t-and F-value did not exceed the theoretical value. These results indicated that there was no significant difference between the proposed and 3,3'-diaminobenzidine methods.

Conclusion

The proposed method offered the advantages of simplicity, rapidity, sensitivity and reasonable selectivity. In addition, it does not require heating or

Table (3) : Tolerance limits in the determination of $4 \mu\text{g ml}^{-1}$ of Se (IV) or Te (IV) with XO.

| Ion added | Amount tolerated / μg | |
|--|----------------------------------|---------|
| | Se (IV) | Te (IV) |
| CH_3COO^- , NO_3^- , PO_4^{3-} , AsO_4^{3-} | 10000 | 8000 |
| Cl^- , SO_4^{2-} , ClO_4^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ | 8000 | 7500 |
| Na^+ , Ba^{2+} , Mg^{2+} , Sr^{2+} | 6800 | 6000 |
| Ca^{2+} , Li^+ , Cd^{2+} | 5000 | 4800 |
| Al^{3+} , Ga^{3+} , Sn^{4+} | 3000 | 2500 |
| Fe^{3+} , Pd^{2+} , Pt^{2+} | 1500 | 1200 |
| Co^{2+} , Hg^{2+} , Pr^{3+} | 1000 | 750 |
| La^{2+} , Sm^{3+} , Eu^{3+} | 500 | 400 |
| UO_2^{2+} , VO_2^+ | 240 | 180 |
| Sc^{3+} , Y^{3+} , Gd^{3+} | 120 | 100 |
| Zr^{4+} , Th^{4+} | 50 | 40 |
| Bi^{3+} , In^{3+} , Tl^{3+} | 30 | 25 |

Table (4) : Determination of Se (IV) in different samples.

| Sample | Se (IV) added $\mu\text{g ml}^{-1}$ | Certified value of Se(IV) $\mu\text{g ml}^{-1}$ | Se(IV) found* $\mu\text{g ml}^{-1}$ | |
|-------------------|---|---|-------------------------------------|--|
| | | | proposed method | Reported method ²⁶ (DAB) |
| Natural water | 1.5 | - | 1.51 | 1.51 |
| Polluted water | - | - | 0.48 | 0.49 |
| Plant material | - | - | 0.51 | 0.50 |
| Medicated shampoo | - | 35.54 | 35.62 | 35.45 |

* Average of six determinations.

(DAB) : 3,3' diaminobenzidine.

extraction with organic solvent compared to the previous work. Based on the data obtained using the proposed colorimetric method, Se (IV) in ground and polluted water, plant material and medicated shampoo was satisfactorily determined.

References

1. J.R. Shapira, in *Organic Selenium Compounds. Their Chemistry and Biology*, D.L. Klayman and W.H. Gunther (eds), P. 701. Wiley Interscience, New York, 1971.
2. M.I. sitting, *Toxic Metals, Pollution Control and Worker Protection*. Noyes Data Corporation, Park Ridge, USA., 1976.
3. H. Afsor, R. Apak and Tor, *Analyst*, **114**, 1319, (1989).
4. K.N. Ramachandran, R. Kaveeshwar and V.K. Gupta, *Talanta*, **40**, 781, (1993).
5. R. Manish, K.N. Ramachandran and V.K. Gupta, *Talanta*, **41**, 1623, (1994).
6. M.N. Pathare and A.D. Sawant, *Anal. Lett.*, **28**, 317, (1995).
7. K. Johansson, O. Andersson and A. Olin, *Analyst*, **120**, 423, (1995).
8. A. Ramesh, T.V. Ramakrishna, and M.S. Subramanian, *Bull. Chem. Soc. Jpn.*, **67**, 2121, (1994).
9. T. Kubota, K. Suzuki, T. Okutani, *Talanta*, **42**, 949, (1995).
10. A. Safavi and A. Afkhami, *Anal. Lett.*, **28**, 1095, (1995).
11. M.M. Zareh, A.S. Amin and M. Abd El-Aziz, *Electroanal.*, **7**, 587, (1995).
12. J.K. Jain, D.C. Pandey, K.C. Joseph and K. Satyanarayana, *J. Indian Chem. Soc.*, **54**, 405, (1977).
13. N. Singh, R. Kumar and R.C. Agarwal, *Curr. Sci.*, **46**, 851, (1977).
14. R.T. Egikyan and D.S. Gaibakyan, *Armenian. Khim. Zh.*, **26**, 909, (1973).
15. S. Dinidi and V.V. Reddy, *Chem. Anal. (Warsow)*, **39**, 89, (1994).
16. P. Liang and J. Linhua, *Huaxue Fence*, **25**, 118, (1989).
17. A. Hassan, *Monatsh. Chem.*, **122**, 605, (1991).
18. M. Dave, S.C. Levale and K.S. Pitre, *J. Inst. Chem.*, **63**, 167, (1991).
19. I.M. Al-Daher, F.A. Fattah and K.A. Najm, *Analyst*, **115**, 645, (1990).
20. L.S.A. Dikshitulu and D. Satyanarayana, *Talanta*, **22**, 313, (1975).
21. R. Kobayashi and K. Imaizumi, *Anal. Sci.*, **7**, 447, (1991).
22. J. Kinnunen and B. Wennestrand, *Chemist-Analyst*, **46**, 92, (1957).
23. V. Mach, S. Kotrly and K. Vytras, *Chem. Papers*, **41**, 57, (1987).

24. V. Kubà, I. Jancarova and L. Sommer, *Chem. Listy*, **83**, 424, (1989).
25. V. Mach, S. Kotrly and K. Vytras, *Chem. Papers*, **43**, 377, (1989).
26. M.L. Cabello- Tomas, and T.S. West, *Talanta*, **16**, 781, (1969).
27. J. Dolezal and L. Sommer, *Scripta Fac. Sci. Nat. Univ. Nasaryk. Brun.*, **21**, 3, (1991).
28. A. Hrdlicka, J. Havel, C. Moreno and M.Valiente, *Anal. Sci.*, **7**, 925, (1991).
29. J. Havel, C. Moreno, A.Hrdlicka and M.Valiente, *Talanta*, **41**, 1251, (1994).
30. B.C. Russel, *Talanta*, **14**, 957, (1967).

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