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Spectrophotometric Determination of Tellurium in Various Samples using Salycilidine-2-Aminophenol-4-Sulphonic Acid (SASAC)

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Abstract
A rapid, simple and sensitive spectrophotometer method for the determination of traces and ultra-traces of tellurium(IV) were studied. These method were based on using Salycilidine-2-Aminophenol-4-Sulphonic Acid (SASAC) as an analytical reagent The reagent has been synthesized and characterized using IR, 1H NMR. The reagent forms dark yellow colored complex with Te (IV) showing maximum absorbance at 432 nm in borates buffer medium (pH= 8). Beer's law were obeyed in the concentration range 0.31-20.41 µg mL^{-1}, having molar absorptivity and Sandal's sensitivity of $1.43\times10^{+4}$ L mol^{-1} cm^{-1} , and 0.0018 µg cm^{-2}, respectively. The optimum reaction conditions and other analytical parameters were investigated to enhance the sensitivity of the present method. The tolerance limit of various ions with this method has been studied. The proposed method was applied for the analysis of tellurium in water samples, plant materials and soil samples. The results obtained by the proposed method were superior to the reported method. The performances of proposed methods were evaluated in terms of student's '*t*'-test and variance ratio '*f*'-test which indicates the significance of proposed methods over reported methods.
Keywords: Tellurium determination, spectrophotometry, (SASAC) . Environmental samples

Introduction

Tellurium is a poisonous element in living biological systems, it can be accumulated in kidney, heart, liver and spleen, and induce the degeneracy of liver and kidney in excess of 0.002 g kg^{-1} (Chai 1978). The content of tellurium in kidney, liver and muscle is 0.07, 0.014 and 0.017 mg kg^{-1}, respectively (Chai *et al*. 1994). In view of the extremely low concentration in biological samples, it is necessary to develop sensitive, precise and accurate analytical methods for tellurium determination in biological specimens. Various analytical methods have been developed for the determination of trace tellurium in urine, determined tellurium in urine by graphite furnace atomic absorption spectrometry after solvent extraction and hydride generation atomic absorption spectrometry, an electrothermal atomic absorption spectrometry (EAAS) method using platinum as a modifier for tellurium determination in urine(Kobayashi *et al*. 1991& Kobayashi *et al*. 1991), plasma and tissues (Stiddik *et al*. 1988). Because of the volatile nature of tellurium, a suitable chemical modifier should be selected when using EAAS. We described a method for determination of tellurium in urine by hydride generation atomic fluorescence spectrometry (HGAFS) after solvent extraction (Lü *et al*. 2000), determined tellurium in urine by isotope dilution gas chromatography–mass spectrometry using (4-fluorophenyl) magnesium bromide as aderivatizing agent and a comparison with EAAS (Aggarwal *et al*. 1994).Te (IV) and Te (VI) were determined by employing dispersive liquid-liquid micro extraction combined with electro thermal atomic absorption spectrometry **(**Najafi *et al*. 2010 **),** flow-injection hydride generation atomic absorption spectrometry, the linear range for the calibration curve was 0.5-12 ng/ ml **(**Hui-Ming *et al*. 2002**)**, Spectrophotometric Determination of Tellurium in Sea Water and Synthetic Alloys (Sadallah et al. 2013), Kinetic-Spectrophotometric (Ensafi et al. 2003), Spectrophotometric based on its catalytic effect (Ensafi et al. 2002), in milk by hydride generation atomic fluorescence spectrometry (Cava-Montesinos et al. 2004), ICP-MS (Thiel et al. 2004)

The main purpose of this paper is to establish a sensitive, simple and reproducible method for determination of trace tellurium . The proposed method has been applied to the determination of trace tellurium in Environmental samples with satisfactory result.

2. Experimental

2.1. Apparatus

A Jasco V–530 UV–VIS spectrophotometer (Japan) with 1 cm quartz cells was used for all absorbance measurements under the following operating conditions: scan speed medium (400 nm/min), scan range 200–1100 nm and slit width 2 nm. Spectra were automatically obtained by Jasco system software. pH measurements were made with ORION 250A (USA) with combined glass pH electrode.

NMR Spectrometry Bruker 400MHz , FT-IR 4100 (Fourier transform infrared spectrometer) Jasco the results of the suggested method were coincidental with the analysis data of the same samples with the Hydride Generation-Atomic Absorption technique as a comparative method

2.2. Reagents and materials
All chemicals used were of analytical-reagent grade of the highest purity available procured from Merck. Doubly distilled de-ionized water was used throughout the experiment.

2.3. Preparation of reagent (SASAC)
SASA was prepared In flask equipped with a reflux condenser and an efficient stirrer is placed 500 mL of absolute (99.8%) ethanol. To this is added (0.012 mol) 2-Aminophenol-4-Sulphonic Acid, and, after solution is complete,.(0.012 mole) of Salicylaldehyd and catalytic added. The mixture is heated 2.5 hours, At the end of the reaction time, The base shiffe separates almost immediately.

The SASA is filtered from the cooled solution, washed well with ethanol, and partially dried. Redefined recrystallized by ethanol and water Until the stability of the Melting point 255ºC.

The purity of the synthesized reagents is assayed by HPLC technique(Figure 1). The yield of (90 %) (Figure 1).

Figure 1. Synthesis of SASAC.

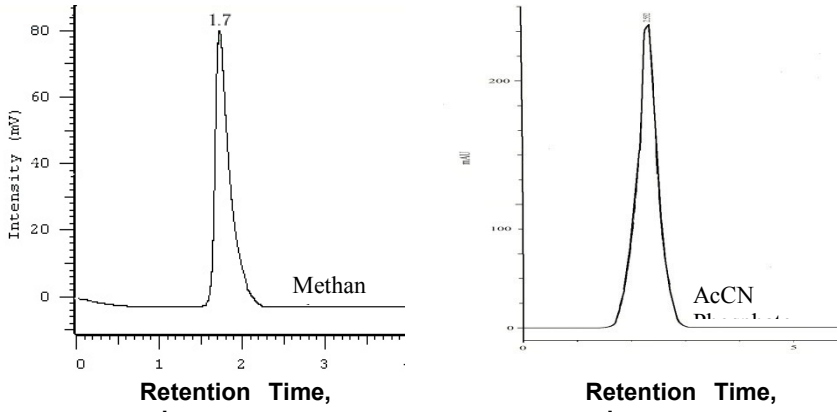
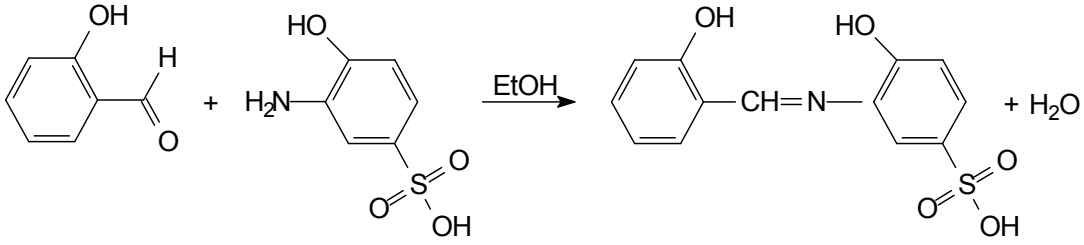


Figure 2. purity of the synthesized reagent by HPLC

2.4. Characterization of reagent SASAC
The reagent has been synthesized and characterized by IR, 1HNMR data. Infrared spectrum of SASAC shows bands at 3435 , 2684 - 3065, 1243, 1609, respectively corresponding to ν (O-H)-C=C-N, ν OH-C=C-CH, ν C-H aromatic, ν (S= O), ν (HC =N) (Figure 3).

H1NMR spectrum of SASAC ($CDCl_3$+DMSO) showed at 6.9-8.4 (10H), 8.9 (1H), due to CH=N,. The molecular formula of the reagent is $C_{13}H_{11}NSO_4$ (M.Wt, 277).

2.5. pKa values of reagents
The pKa values were determined by recording the UV-Visible spectra of 1×10^{-4}M solutions of the reagent at



various pH values and by taking the arithmetic mean of the values obtained from the measurements at different wave lengths determined spectrophotometrically depended on reference analytical methods (half height, Limit absorbance and Colleter's). The values of deprotonation of SASAC were (3.88, 7.76 and 9.76)

2.6. SASAC solution
A 1×10^{-2}M solution was prepared by dissolving 0.294g of SASAC in 100 ml of water., The reagent solution is stable for one week.

2.7. Te (VI) solution

Working solutions of the Tellurium(VI) oxide was prepared by dilution of the corresponding standard solutions 1000 mg L^{-1} (Merck) with doubly - deionised distilled water, Dilute solutions were prepared from this stock solution.

2.8 General Procedure

Stock solution containing of tellurium were transferred into 25 mL calibrated flask and 1 mL of SASAC reagent were added followed by 1 mL of borates buffer. The mixture was heated at temperature (90°C), allowed to stand for 1 min for the completion of the reaction. The contents were diluted up to the mark with doubly-deionised distilled water and the absorbance was measured at 432 nm against the corresponding reagent blank and the calibration graph was constructed

2.9. Procedure for Preparation of various samples

2.9.1 Determination of tellurium in natural water samples

The proposed method were employed for different natural water samples (200 mL) collected. The samples were used directly to measure the tellurium(IV) contents by the proposed methods after filtered with cellulose membrane of pore size 0.45 µm as mentioned in literature 24 and determined by above general procedure.

2.9.2 Determination of tellurium in vegetable samples

5 g of finely chopped fresh tomato samples each were placed in a 500 mL beaker and 10 mL of a 1:1 (v/v) mixture of concentrated sulfuric acid and nitric acid were added. This solution was heated, until the mixture was clear. Then the solution was filtered and concentrated to 5 mL, cooled and diluted up to 50 mL with doubly-deionised distilled water. The general procedure was employed to 1 mL of this solution for analysis of tellurium.

2.9.3 Determination of tellurium in soil sample

A known weight of tellurium was mixed with 20 g of soil sample, fused with 1:1 sodium carbonate and potassium nitrate mixture in a nickel crucible and extracted with water. The filtrate of the extract was treated with 20 mL of 10 mole L^{-1} hydrochloric acid and thenheated to expel chlorine and oxides of nitrogen. The solution was further diluted with water to give a suitable concentration of tellurium. An aliquot of the stock solution was passed through the cation exchange resin (Amberlite) to remove the cation ions present in soil. The tellurium contents were determined as described in the general procedure

2.10. Preparation of the calibration graph

An aliquot of the stock solution containing 1.0-200 µM of tellurium (IV) was transferred into a 25 mL volumetric flask. The solution was diluted up to the mark with distilled water and mixed well. The absorbance of the solution was measured after about 1 minutes at 432 nm against a reagent blank. The amount of tellurium in the sample solution was then deduced from the calibration graph.

3. RESULTS AND DISCUSSION

Tellurium reacts with Salycilidine-2-Aminophenol-4-Sulphonic Acid (SASAC) at pH =6 (1:1) and gives dark yellow colored complex. The complex has a maximum absorbance at 432 nm. The optimum reaction conditions for the quantitative determination of the metal-ligand complex was established through a number of preliminary studies, such as the effect of acidic medium, reagent concentration, interference of foreign ions, in order to develop a rapid, selective and sensitive spectrophotometric method for the determination of Tellurium (IV) at microgram levels.

3.1. Absorption spectra of the reagent and Te (IV)-SASAC complex

Absorption spectra of Te (IV)-SASAC complex and reagent show maximum absorbance at 442 nm and 286 nm and 371nm, respectively (Figure 4). The reagent showed minimum absorbance at the wavelength of maximum absorbance of the complex. Hence, all the spectral measurements of the complex were therefore carried out at 360 nm .

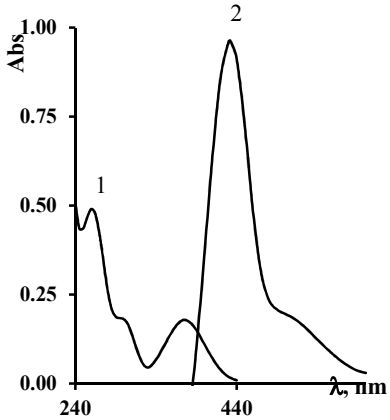


Figure 4. (1) Absorption spectra of reagent
(2) Absorption spectra of Te-SASAC complex

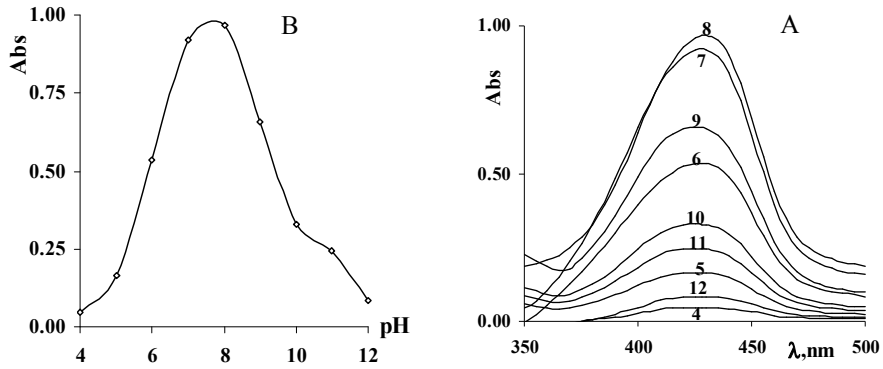
3.2. Optimization of reaction conditions

The spectrophotometric properties of the colored product as well as the different experimental parameters affecting the color development and its stability were studied and optimized by changing each variable in turn, while keeping all others constants. In all experiments.

3.3. Effect of pH concentration

The effect of pH on the peak height of tellurium(IV) at different concentrations was investigated with a fixed reagent concentration in the pH range of 3.0 – 10 and the peak height was measured for each concentration level of tellurium(IV). At all concentration levels of Te(IV), maximum peak heights were found between pH 7 – 8.5. Therefore, a pH 8.0 was selected for further studies.achieved. Therefore, 1 ml of borates buffer was used for the better results (Figure 5).

Figure 5. **A** - Absorption spectra in varing pH.
B - the varing pH effect on the absorbance of the formed complex Te(IV)-SASAC



3.4. Effect of reagent concentration

All analytical studies were therefore, carried out at (pH=8). Different volume of molar excess of SASAC was added to fixed Te (IV) concentration and the absorbance's were measured adopting the standard procedure. It was observed that 10 fold molar excess of reagent with respect to metal ion is necessary to get maximum absorbance. Hence, a 10 fold molar excess of reagent was used for further experimental studies. The absorbance of the solution was measured at different time intervals to ascertain the time stability of the color complex.

3.5. Effect of temperature Time on colored product

The effect of the temperature on the product was studied at different temperatures; it was found that the colored product was stable for more than 10 days in the temperature range of 80 – 95 ^{o}C. So, the temperature at 90 ^{0}C was selected as optimum for maximum color development.Tellurium (IV) can react with SASAC to form a complex in one min at temperature (90°C), and is stable at room temperature. The stability of the absorbance at least 10 days..

3.6. Analytical method validation

3.6.1. Calibration, graph reproducibility and detection limit

Using the optimized composition and conditions described above . The effect of the Te concentration was studied over 1.00-200.0 µM for convenience of the measurement. The calibration curves gave an excellent linear for (2.5-160.0µM), (0.31-20.41µg/mL), as shown in (Figure 6) at 432nm, The molar absorption coefficient and the Shandell's sensitivity were found to be 1.4 x 10^4 L mol^{-1} cm^{-1} and 0.0081 µg cm^{-2} of Te respectively. The selected analytical parameters obtained are summarized in Table 1.

3.6.2. Precision and accuracy

The precision and accuracy of the method was studied by analysing solutions containing known amounts of Te (IV) within the Beer's law limit. Percentage relative standard deviation (RSD %) as precision and percentage recovery as calculated and showed in Table 2. The values of relative standard deviations for different concentrations of Te determined from the calibration curves. These results of accuracy and precision show that the proposed method have good repeatability and reproducibility. The lower values of relative standard deviation (%) indicated the high accuracy of the method.

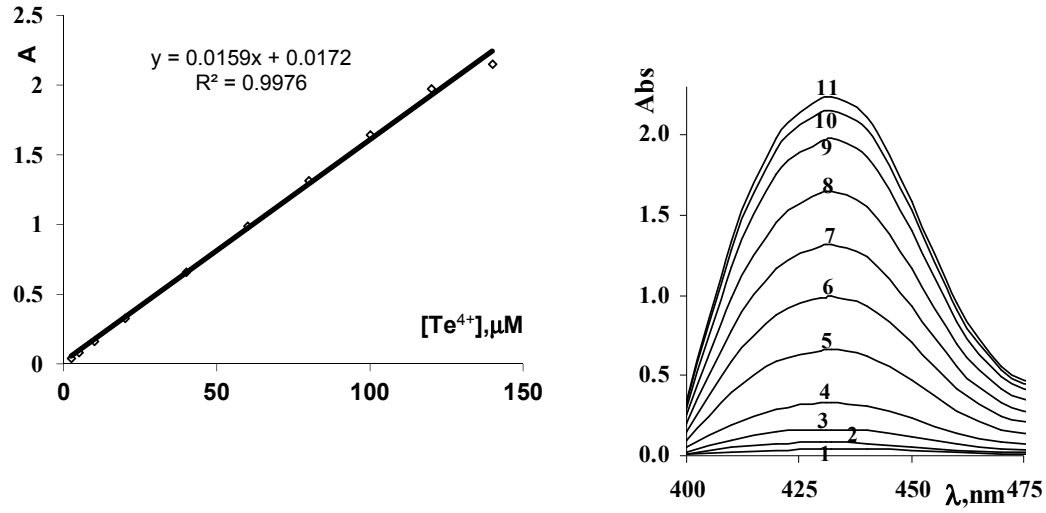


Figure (6). - Absorption spectra in varing Te concentration
The linear range between absorbance formed complex and Te concentration

Table.1. Analytical characteristics of method

Parameters	
Wavelength / λ_{max} (nm), complex	432
Wavelength / λ_{max} (nm), reagent	260,371
Solvent	Water, pH=8
Time / min	1.0
Temperature /°C	90°C
Mole of reagent required mole of metal ion for full color developed	10 Fold
Composition of complex as obtained in Job's and molar ratio methods (M:L)	1 : 1
Molar absorption Coefficient/ L $mol^{-1}cm^{-}$	1.4×10^4
Linear range/µg mL^{-1}	0.31-20.41
Detection limit /µg mL^{-1}	0.10
Sandell's Sensitivity /µgcm^{-2}	0.0081
Relative Standard Deviation	2.50-0.66
Regression Co-efficient	0.997
Slope	0.0159

Table 2. Accuracy and precision for the determination of Te in pure soluation

$[Te^{+4}]$, µM*			Confidence limit	Recovery %
Taken	Found[a]	RSD %	**$CL_{95\%}$,µM**	
10	9.71	2.50	9.71±0.30	97.11
15	14.73	1.87	14.73± 0.34	98.20
25	25.29	1.54	25.29± 0.48	101.15
50	50.17	0.85	50.17± 0.53	100.34
70	70.06	0.66	70.06± 0.57	100.08

[a]Five independent analyses**.**

3.6.3. Effect of diverse ions

The effect of various species on the determination of Te (IV) was investigated. The tolerance limit was taken as the amount that caused ± 2% absorbance error in determination of 5 µg mL^{-1} of tellurium. The results were shown in Table 3.

Table 3. Effect of foreign species on the determination of 5 µg mL^{-1} of tellurium (IV).

Species	Tolerance limit, µg mL^{-1}	Species	Tolerance limit, µg mL^{-1}
EDTA	10040	[b]Cu^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+}	75
Na^{+}, Mg^{2+},Cl^{-}, NO_3^{-}, F^{-}, $CHCOO^{-}$, CO_3^{2-}, K^{+}	2214	Zn^{2+}, Pb^{2+b}, SO_3^{2-}, NO_3^{-}, Cr^{3+}, As^{5+}	45
Ba^{2+}, SO_4^{2-}, CN^{-}, SCN^{-}, Tartarate	1120	Fe^{2+a}, S^{2-}	40
PO_4^{3-}, Al^{3+}, Cd^{2+}, NO_2	845	Se^{+4}	1000

a Can be masked up to 800 µg mL^{-1} by the addition of 3 mL of 2 % sulphamic acid.
b Can be masked up to 100 µg mL^{-1} by the addition of 3 mL of 5% EDTA.

The results in the above table indicate that a high Tolerance limit, were Observed due to the competition of these ions with Te (IV) for the reagent(appearance of yellow colour) there by depleting the reagent available for the Te (IV) ion

3.6.4. Composition and stability constant of the complex

Job's method of continuous variation and molar-ration methods were applied to ascertain the stoichiometric composition of the complex. It was found that SASAC forms 1:1 complex with Te (IV) as shown in the (Figure7).

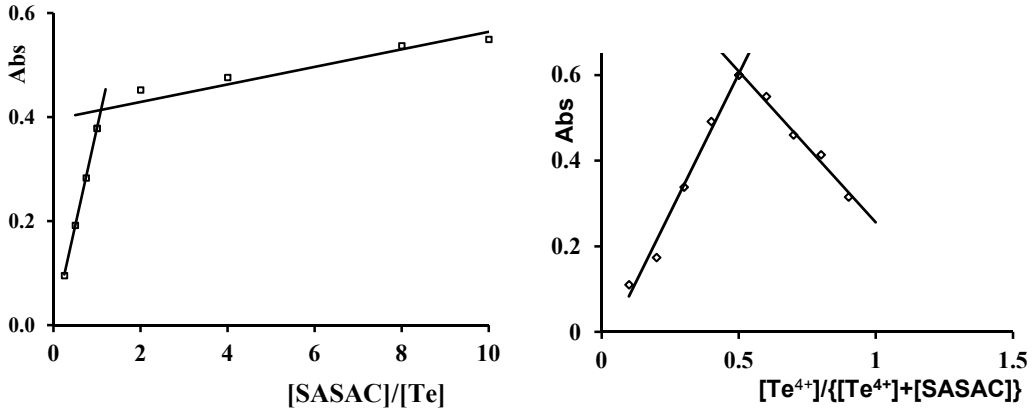


Figure.7. continuous variation and molar-ration methods
Te (IV)-SASAC. Te (VI) and SASAC,1 ×10^{-3}M

3.6.5. Application

The proposed spectrophotometric method is applied for the determination of Te (IV) in various samples. A known aliquot of the above sample solutions were taken and the Tellurium content was determined as described is given in the general procedure, and the results of the suggested method were coincidental with the analysis data of the same samples with the Hydride Generation-Atomic Absorption technique as a comparative method Table 4.

Table (4): Determination of traces of tellurium(IV) in various samples
n = 5 , α = 0.95

Samples	Proposed method					Reported method		
	Tellurium added , µg	Tellurium found, µg	Recovery %a	*t*-test	*f*-test	Tellurium added , µg	Tellurium found, µg	Recovery %
Waste water	0.40	0.12 0.51	98.07±0.34			0.40	0.48	96.00±0.34
River water	0.20	0.16 0.358	99.44±0.27			0.20	0.34	97.22±0.21
Tomato	1.30	0.08 1.37	99.27±0.53			1.30	-	
Soil sample	1.90	0.05 1.92	98.46±0.61			1.90	1.85	97.36±0.38

4. CONCLUSION

The author has introduced a new sensitive reagent SASAC for the direct spectrophotometric determination of trace amounts of Te (IV). The proposed spectrophotometric method is simple, highly sensitive and selective for the determination of Te (IV) in water and soil samples when compared with other spectrophotometric methods.. It also offers advantages like reliability and reproducibility in addition to its simplicity instant color development and less interference effect. The results obtained through UV-Visible spectrophotometer have been compared with those obtained through the HG-AAS. The method has been successfully applied for the determination of tellurium in various samples.

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