Low Absorbance Differential Spectrophotometry

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A low absorbance differential spectrophotometry method is proposed. This method is investigated theoretically and experimentally. Its precision and accuracy are compared with those of ordinary spectrophotometry. The results of the proposed method are better than those of normal spectrophotometry in the analysis of the low absorbance samples. In addition, the common problem of the nonlinear relationship between differential absorbance and concentration has been resolved in this method.

The accuracy of differential spectrophotometry is better than ordinary spectrophotometry for the determination of low and high absorbance samples.[1] In the previous low absorbance differential spectrophotometry procedure, a standard solution of greater concentration than the sample is employed instead of the shutter for zeroing the transmittance scale; the full-scale transmittance adjustment is made in the usual way, *i.e.*, with the solvent in the light path. The sample transmittance is then obtained by replacing the solvent with the sample. The effect of this procedure is shown in Fig. 1. If C_x is the analyte concentration in the sample, C_s is the concentration in the standard solution, and A is the measured absorbance, then

$$A = \log \frac{1-10^{-\varepsilon bC_s}}{10^{-\varepsilon bCx}-10^{-\varepsilon bC_s}}$$

A nonlinear relationship exists between differential absorbance and concentration, so its application was limited. In this paper, an alternative low absorbance differential spectrophotometry is proposed. In the procedure, the zero transmittance adjustment is carried out in the usual way having the shutter placed between the source and the detector; the 100% transmittance adjustment, however, is made with the sample to be determined instead of the solvent for the full-scale transmittance adjustment, in the light path. Finally, the sample is replaced by a standard solution of greater concentration than the sample and the relative transmittance is read directly. The effect of this procedure is shown in Fig. 2. In this case

$$A = \varepsilon b(C_s - C_x)$$

A linear relationship exists between differential absorbance and concentration in the sample. Choosing a suitable C_s can bring the transmittance reading into the middle of the scale, where instrumental uncertainties have a minimal effect on the relative concentration error.

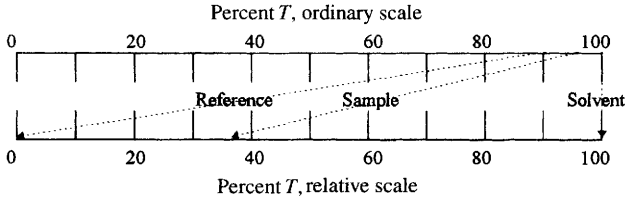

Fig. 1 Low absorbance differential spectrophotometry.

Experimental

Apparatus

A Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer (Perkin-Elmer Inc. USA), equipped with 1 cm path-length quartz cells, was used.

Reagents

All the reagents are of analytical-reagent grade. The iron, nickel and phenol stock standard solutions were prepared by the routine method. A 10% stock solution of 1,10-phenanthroline, a 1% stock solution of biacetyl dioxime, and a 2% stock solution of 4-aminoantipyrine were carefully prepared.

Procedures

Determination of iron standard sample

Into six 25 ml calibrated flasks, 0.00, 0.25, 0.50, 0.75, 1.00, and 1.25 ml of 10 μg ml^{-1} stock solution of iron were added to prepare the standard solutions. Into a seventh 25 ml calibrated flask, 0.60 ml of 1 mg ml^{-1} stock solution of iron was added to prepare the reference solution. Into each of the above calibrated flasks, 2 ml of 0.05 mol l^{-1} NaOH, 1 ml of 30% NaAc, 1 ml of 10% hydroxylamine hydrochloride and 1 ml of 10% 1,10-phenanthroline were added in the given order, heated for 2 min in boiling water and diluted to 25 ml with doubly distilled water after cooling. The differential absorbances of the reference solution against each standard solution were measured at 510 nm. A standard axes graph was obtained by plotting differential absorbance values *versus* the concentration of the standard solutions.

A 0.50 ml sample was then determined using the method described above.

Determination of nickel standard sample

Into six 25 ml calibrated flasks, 0.00, 0.20, 0.60, 0.80, and 1.00 ml of 10 μg ml^{-1} stock solution of nickel were added to prepare

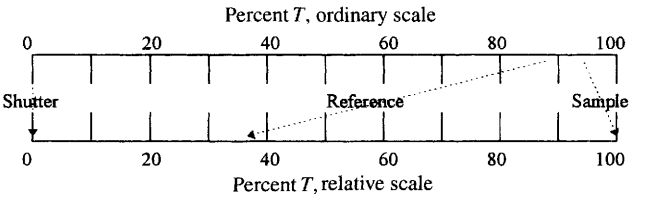

Fig. 2 Proposed new low absorbance differential spectrophotometry.

the standard solutions. Into the seventh 25 ml calibrated flask, 0.50 ml of 1 mg ml^{-1} stock solution of nickel was added to prepare the reference solution. Into the above calibrated flasks, 1 ml of 50% ammonium citrate, 3 ml of concentrated aqueous ammonia, 1 ml of saturated aqueous bromine and 0.4 ml of 1% biacetyl dioxime were added in the given order and then diluted to 25 ml with doubly distilled water after mixing. The absorbances of the reference solution against each standard solution were measured at 445 nm. A standard axes graph was obtained by plotting differential absorbance values *versus* the concentration of the standard solutions.

A 3.00 ml sample was analysed using the proposed method.

Determination of trace phenol in running water

Into six 100 ml calibrated flasks, 0.00, 1.00, 2.00, 3.00, 4.00, and 5.00 ml of 1 μg ml^{-1} stock solution of phenol were added to prepare the standard solutions. Into the seventh 100 ml calibrated flask, 25.00 ml of 10 μg ml^{-1} stock solution of phenol was added to prepare the reference solution. Into the above calibrated flasks, 2.50 ml of 0.5 mol l^{-1} NH_4OH, 0.5 ml of pH 7.9 phosphate buffer solution and 1 ml of 8% $K_3Fe(CN)_6$ were added in the given order. They were diluted to 100 ml with doubly distilled water after mixing and then laid up for 60 min. The differential absorbances of the reference solution against each standard solution were measured at 500 nm. A standard axes graph was obtained by plotting the differential absorbance values *versus* the concentration of the standard solutions.

An aliquot (5 ml) of distillate of the running water was taken by the method given in ref. 2 and was determined using the method described above.

Results and Discussion

Comparison of the Results Determined by the Proposed Method and Ordinary Spectrophotometry

The results of the analysis of 10 equal concentration iron standard samples determined by the two methods are shown in Table 1. The RSD of proposed method is 0.20% and the RSD of ordinary spectrophotometry is 1.89%.

The results of the analysis of 10 different concentration iron standard samples determined by the two methods are shown in Table 2.

The results of the analysis of 10 equal concentration nickel standard samples determined by the two methods are shown in Table 3. The RSD of proposed method is 0.30% and the RSD of ordinary spectrophotometry is 3.68%.

The results of the analysis of 10 different concentration nickel standard samples determined by the two methods are shown in Table 4.

The results of the recovery experiment for trace phenol in water by the two methods are shown in Table 5. The recovery of trace phenol in water by the proposed methods is better than that by the ordinary method.

Conclusion

It can be seen from the results of the iron standard sample, nickel standard sample and trace phenol in running water, that

Table 1 Results of 10 equal concentration iron standard samples analysed by the proposed method and ordinary method

Sample no.	1	2	3	4	5	6	7	8	9	10
Differential absorbance determined by proposed method	0.430	0.429	0.428	0.428	0.430	0.428	0.428	0.429	0.429	0.430
Absorbance determined by ordinary method	0.046	0.044	0.044	0.045	0.044	0.045	0.044	0.046	0.044	0.044

Table 2 Results of 10 different concentration iron standard samples analysed by proposed method and ordinary method

		Proposed method			Ordinary method		
Sample no.	Amount of iron prepared/ ng ml^{-1}	A^*	Amount of iron determined/ ng ml^{-1}	Relative error (%)	$A^\dagger$	Amount of iron determined/ ng ml^{-1}	Relative error (%)
1	40	0.432	41	2.5	0.006	42	5.0
2	80	0.425	78	−2.5	0.014	84	5.0
3	120	0.417	119	−0.8	0.023	121	0.8
4	160	0.409	158	−1.3	0.031	153	−4.4
5	200	0.399	201	0.5	0.041	196	−2.0
6	240	0.391	239	−0.4	0.049	242	0.8
7	280	0.385	282	0.7	0.058	285	1.8
8	320	0.377	324	1.3	0.066	329	2.8
9	360	0.368	359	−0.3	0.075	354	−1.7
10	400	0.362	402	0.5	0.085	401	0.2

* Differential absorbance determined by proposed method. † Absorbance determined by ordinary method.

Table 3 Determination results of 10 equal concentration nickel standard samples analysed by the proposed method and ordinary method

Sample no.	1	2	3	4	5	6	7	8	9	10
Differential absorbance determined by proposed method	0.425	0.424	0.425	0.426	0.424	0.423	0.427	0.423	0.424	0.425
Absorbance determined by ordinary method	0.044	0.045	0.044	0.046	0.048	0.048	0.048	0.047	0.048	0.048

Table 4 Results of 10 different concentration nickel standard samples determined by proposed method and ordinary method

		Proposed method			Ordinary method		
Sample no.	Amount of nickel prepared/ ng ml^{-1}	A^*	Amount of nickel determined/ ng ml^{-1}	Relative error (%)	$A^\dagger$	Amount of nickel determined/ ng ml^{-1}	Relative error (%)
1	40	0.510	41	2.5	0.010	42	5.0
2	80	0.501	82	2.5	0.019	77	−3.8
3	120	0.492	119	−0.8	0.030	113	−5.8
4	160	0.483	160	0	0.044	161	0.6
5	200	0.470	202	1.0	0.050	191	−4.5
6	240	0.465	239	−0.4	0.061	237	−1.3
7	280	0.456	278	−0.7	0.070	276	−1.4
8	320	0.448	319	−1.3	0.081	323	0.9
9	360	0.439	364	1.1	0.090	365	1.4
10	400	0.430	403	0.8	0.101	398	−0.5

* Differential absorbance determined by proposed method. † Absorbance determined by ordinary method.

Table 5 Results of trace phenol recovery experiment determined by the proposed method and ordinary method

		Proposed method			Ordinary method		
Sample no.	Amount of phenol prepared/ ng ml^{-1}	A^*	Amount of phenol determined/ ng ml^{-1}	Recovery (%)	$A^\dagger$	Amount of phenol determined/ ng ml^{-1}	Recovery (%)
1	—	0.382	150	—	0.012	150	—
2	75	0.427	226	101.3	0.036	229	105.3
3	80	0.438	229	98.9	0.048	233	103.8
4	85	0.446	237	102.4	0.054	233	97.6
5	90	0.457	239	98.9	0.067	234	93.3

* Differential absorbance determined by proposed method. † Absorbance determined by ordinary method.

the precision and accuracy of proposed method are better than those of the ordinary spectrophotometry in the determination of low absorbance samples. In addition, a linear relationship exists between differential absorbance and concentration in the proposed method, so the proposed method can be easier to use than traditional low absorbance differential spectrophotometry.

References

1 Reilley, C. N., and Crawford, C. M., *Anal. Chem.*, 1955, **27**, 716.
2 APHA-AWWA-WPCF *Standard Methods for the Examination of Water and Wastewater*, 17th edn., 1989, 705–754.

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