

SPECTROPHOTOMETRIC DETERMINATION OF SOME AROMATIC DIAMINES USING SODIUM SULPHIDE AND AN OXIDANT

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في هذا البحث تم أستنباط طريقة لونية بسيطة ومتخصصة للتقدير الكمي لبعض المركبات العطرية ثنائية الأمين وتعتمد هذه الطريقة على تفاعل كبريتيد الصوديوم مع محلول مائي للمركب في وجود عامل مؤكسد عند درجة حرارة الغرفة فيتكون لون أزرق هو عبارة عن صبغة أزرق الميثيلين أو مشتقاتها.

وقد طبقت هذه الطريقة على ثلاث مشتقات للبارافينالينات ثنائية الأمين وتم قياس الألوان الناتجة عن 597، 665، 670 ن.م للثلاث مركبات.

تم أيضا في هذا البحث دراسة تأثير جميع متغيرات التفاعل مثل نوع العامل المؤكسد وقد جربت عدة عوامل مؤكسدة منها الحديد الثلاثي، والسيريوم الرباعي، ن-بروموسكسينيميد وكذلك تأثير تراكيز الكواشف، درجة الحرارة، المذيب المناسب، وثبات اللون المتكون. هذا وقد تم الحصول على اللون في ظرف خمس دقائق وظل ثابت لمدة لا تقل عن 24 ساعة بإستخدام الماء كمذيب. وبإستخدام أحسن الظروف المختارة تم رسم المنحنى القياسي الذي وجد أنه يتبع قانون بيرير وأن الجزء المقطوع من محور ص صغير جدا.

وقد طبقت هذه الطريقة بنجاح في التقدير الكمي للبارافينالينات ثنائية الأمين في عينات من ماء نهر النيل وكذلك في وجود بعض الأمينات العطرية الأخرى بدرجة استرجاع عالية. بالإضافة إلى ذلك قد تم فصل نواتج التفاعل والتعرف عليها عن طريق التحليل الدقي لمكوناتها كذلك قياس طيف الأشعة فوق البنفسجية وتحت الحمراء.

A simple and selective colorimetric method was developed for quantitative determination of aromatic diamines; p-phenylenediamine, N,N-dimethyl p-phenylenediamine and N,N-diethyl-p-phenylenediamine. The method is based on the reaction of sodium sulphide with an aqueous solution of the diamine in presence of an oxidant at ambient temperature to form a methylene blue or ethylene blue like dyes. Absorption maxima of 597, 665 and 670 nm were obtained for the three compounds; respectively. Different oxidizing agents were tried e.g. Ce(IV), Fe(III) and N-bromo-succinimide (NBS). The color was developed within 5 minutes and remained stable for at least 24 hours. Linear calibration graphs with very small intercepts were obtained. The proposed method was applied successfully for determination of aromatic diamines in spiked water samples and in presence of other aromatic amines and excellent recoveries were obtained. Reaction products have been isolated and identified using microanalysis, UV and IR spectrometric methods.

INTRODUCTION

p-Phenylene diamine (PPDA), and its alkyl derivatives; N,N-dimethyl-p-phenylenediamine (N,N DMPPDA) and N,N diethyl-p-phenylene diamine (N,N, DEPPDA) are valuable chemicals in many areas of industry.¹ In addition these

compounds are used as reagents for hydrogen sulphide, uric acid, acetone and for peroxide determination.^{1,2}

The physiological activities of these compounds make them of interest in biological field. Several of diaminic constituents present in hair dyes have been toxic and even

carcinogenic.³ The effects and analysis of these compounds have been extensively studied.⁴ Water pollution by these compounds is possible (from industrial sewage or traditional effluents) and necessitates a rapid and sensitive method for their analysis. Among the methods used for their analysis are titrimetric,⁵ spectrophotometric^{6,7} and chromatographic^{3,8,9} techniques. In addition chemiluminescence methods of analysis were used for determination of these compounds.¹⁰ Most of these methods suffer from interference of other amine constituents.

N,N-Dimethyl-*p*-phenylenediamine has been used before for the determination of sulphide and sulphide producing compounds in the presence of Fe(III) through formation of methylene blue dye.² In this work the applicability of the principle of this reaction for the determination of aromatic diamines using sodium sulphide and Fe(III), Ce(IV) or NBS as oxidants was investigated. As a result, a rapid, sensitive and selective method for determination of those compounds was developed.

EXPERIMENTAL

Apparatus

- A Varian Model DMS100 UV-Visible spectrophotometer, connected to Varian/Model DS15 data station, connected to Hewlet Packard 82905B printer.
- FTIR spectrophotometer Model 1500, equipped with data station, printer plotter Model PPI and central processing unit 1502, all by Perkin Elmer Co.
- Elemental microanalysis was performed by Perkin Elmer, 2400, CHNO Elemental Analyzer.

Materials and Reagents

PPDA sulphate (Riedel De Haen Hanover), N,N DMPPDA dihydrochlorides (BDH, Chemicals Ltd, Poole, England), N,N DEPPDA (Koch-Light Laboratories Ltd. Poole, England), *o*-phenylenediamine sulphate (Koch-Light-Laboratories Ltd., England), *m*-phenylene diamine (BDH, Poole, England); the purity of the compounds was checked using TLC testing

where only one spot for each diamine was produced; N-bromosuccinimide; (Merck, Darmstadt, Germany). All other chemicals and solvents were Analytical Reagent grade. Distilled water was used throughout this work.

Reagent solutions

- Sodium sulphide 1% (w/v) aqueous solution.
- Fe(III) 5% (w/v) aqueous solution.
- Ce(IV) 1% (w/v) solution in 5M H₂SO₄.
- NBS 1% (w/v) aqueous solution.

Standard preparation

Weigh accurately 0.1 gm of each diamine and dissolve in a separate 100 ml flask with distilled water. Complete to volume with the same solvent. Further dilutions were made to obtain 50 µg/ml of each compound. The solutions have to be protected from light in a refrigerator.

General assay procedure

Transfer 5 ml of each diamine into a 50 ml volumetric flask. Add 5 ml sulphide solution followed by 5 ml Fe(III), Ce(IV) or NBS aqueous solution. Stopper the flask and shake for about 30 sec. Allow to stand for 5 minutes and dilute to the volume with distilled water. Allow to stand for further 15 minutes and measure the absorbance at 597, 665 and 670 nm for PPDA, N,N DMPPDA and N,N DEPPDA, respectively.

Preparation and identification of the chromogen

Prepare about 500 ml of the colored product of N,N DMPPD with sodium sulphide and Fe(III). To this solution add portionwise saturated aqueous solution of picric acid or perchloric acid and stir the mixture vigorously. Keep the mixture in a refrigerator for 24 hours. Filter the precipitated picrate or perchlorate salt and wash with water several times. Recrystallize from aqueous ethanol. Dry in vacuum desiccator over calcium chloride and subject to microanalysis and IR identification.

Microanalysis data

Are shown in Table 1.

RESULTS AND DISCUSSION

Spectral characteristics

The absorption spectra of the reaction products of PPDA, N,N DMPPDA and N,N DEPPDA with sodium sulphide in the presence of an oxidant e.g. Fe(III) are shown in Figure 1. In addition, Table 2 shows λ_{max} and molar absorptivities of the three compounds using Fe(III), Ce(IV) and NBS as oxidants. From the figure and the table it is clear that the absorption maxima are red shifted with alkyl substitution (665 nm and 670 nm) while the ϵ_{max} are slightly changed.

Effect of sodium sulphide concentration

The effect of changing sodium sulphide concentration on the absorption intensities of solutions containing 5 $\mu\text{g/ml}$ diamine was studied. The absorbances of the produced colors were measured at 597, 665 and 670 nm for PPDA, N,N-DMPPDA and N,N-DEPPDA; respectively. The results are shown in Figure 2 using Fe(III) as representative example of oxidants. The color intensity was initially increased with increasing sulphide concentration reached maximum upon using 0.015% sodium sulphide for PPDA and 0.01% sodium sulphide for both N,N DMPPDA and N,N DEPPDA. Similar results were obtained with other oxidants. Therefore, these concentrations were used in all subsequent work.

Table 1: Microanalysis data of the studied compounds.

Systematic Names	Molecular Formula	M. weight	%C		%H		%N	
			Cal.	Found	Cal.	Found	Cal.	Found
3,7-Bis(dimethyl-amino)-Phenothiazine* perchlorate	C ₁₆ H ₁₈ ClN ₃ O ₄ S	383.5	50.06	50.67	4.69	4.71	10.95	10.98
3,7-Bis(dimethyl-amino)-Phenothiazine** perchlorate	C ₁₆ H ₁₈ ClN ₃ O ₄ S	383.5	50.06	49.65	4.69	4.72	10.95	10.84
3,7-Bis(dimethyl-amino)-Phenothiazine** picrate	C ₂₂ H ₂₀ N ₆ O ₇ S	512.0	51.56	50.91	3.90	3.89	16.40	16.24

* Methylene blue authentic sample.

** Dye resulting from the interaction of N,N-DMPPDA with sodium sulphide and Fe(III) reagents.

Table 2: λ_{max} and molar absorptivities of the reaction products of the diamines with sodium sulphide and Fe(III), Cerium (IV) or NBS reagents.

Diamine	λ_{max} (nm)	Molar absorptivities		
		Fe(III)	Cerium (IV)	NBS
PPDA	597	2.8×10^4	3.6×10^4	8.6×10^3
N,N-DMPPDA	665	2.4×10^4	2.9×10^4	6.0×10^3
N,N-DEPPDA	670	2.1×10^4	2.8×10^4	5.9×10^3

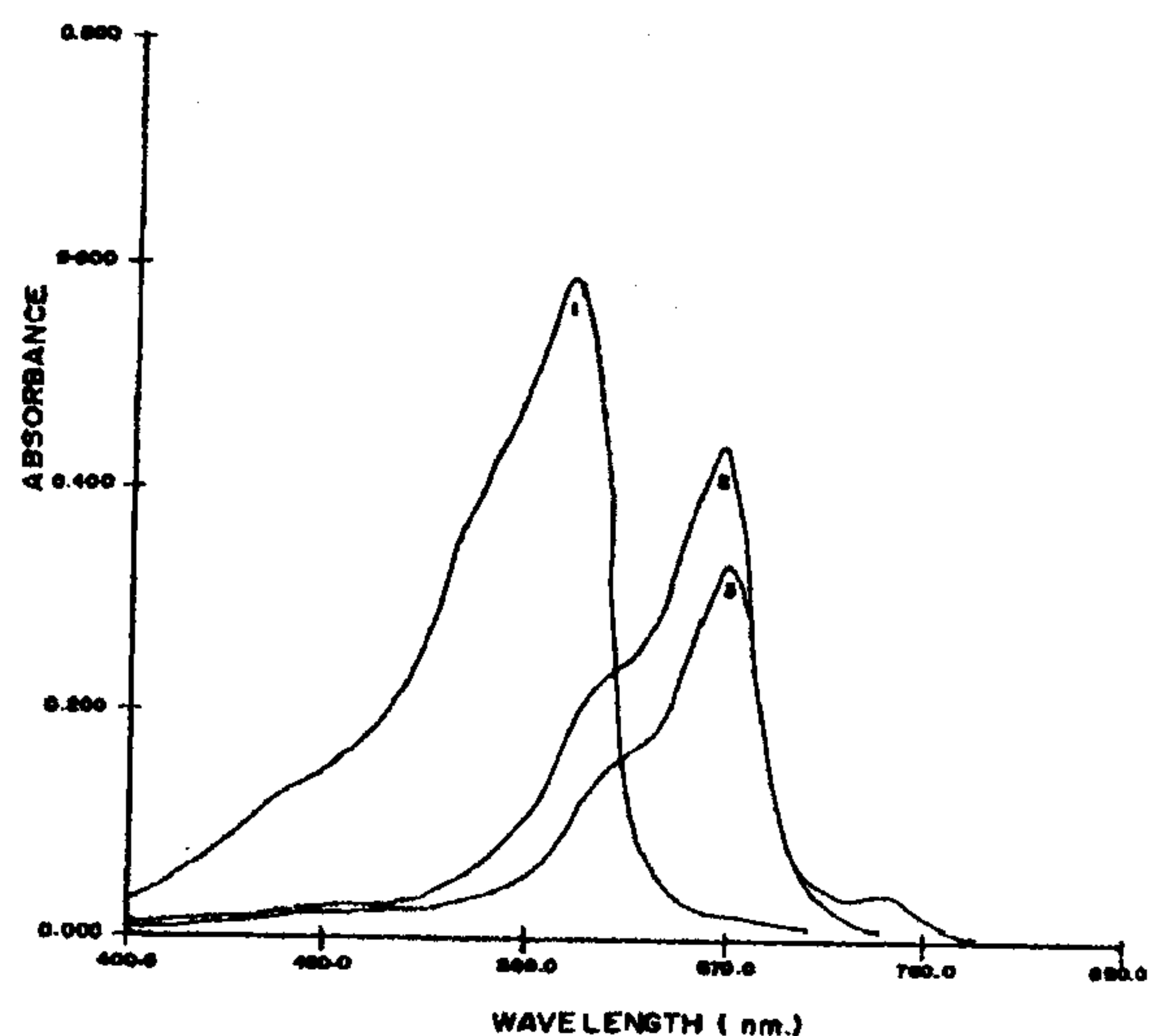


Fig. 1: Absorption spectra for the reaction products of 5 µg/ml: 1) PPDA, 2) N,N-DMPPDA and 3) N-DEPPDA, with Na₂S and Fe(III) reagents.

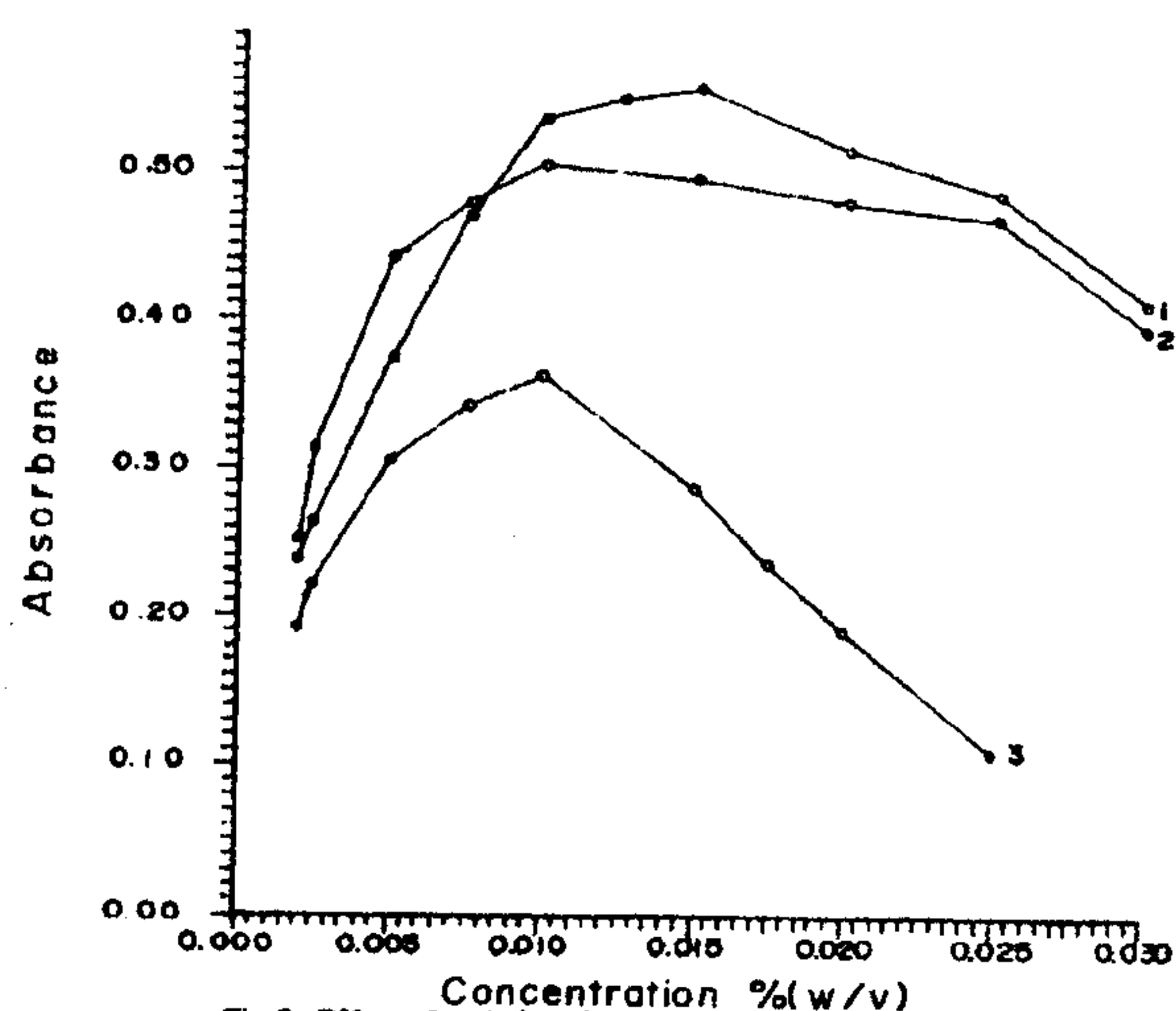


Fig. 2: Effect of variation of Na₂S concentration on the absorption intensity of the reaction product of 5 µg/ml: 1) PPDA, 2) N,N-DMPPDA and 3) N-DEPPDA, with Na₂S and Fe(III) reagents.

Effect of sulphuric acid concentration

The acid concentration is very important for methylene blue reaction.² To find the optimum acid concentration, the reaction was carried out for N,N DMPPDA as representative example using ferric as oxidant with different acid

concentrations. Figure 3 shows that 1 M sulphuric acid gave maximum color intensity for N,N DMPPDA. On the other hand optimum color intensity was obtained upon using 0.15 M sulphuric acid solution for both PPDA and N,N DEPPDA.

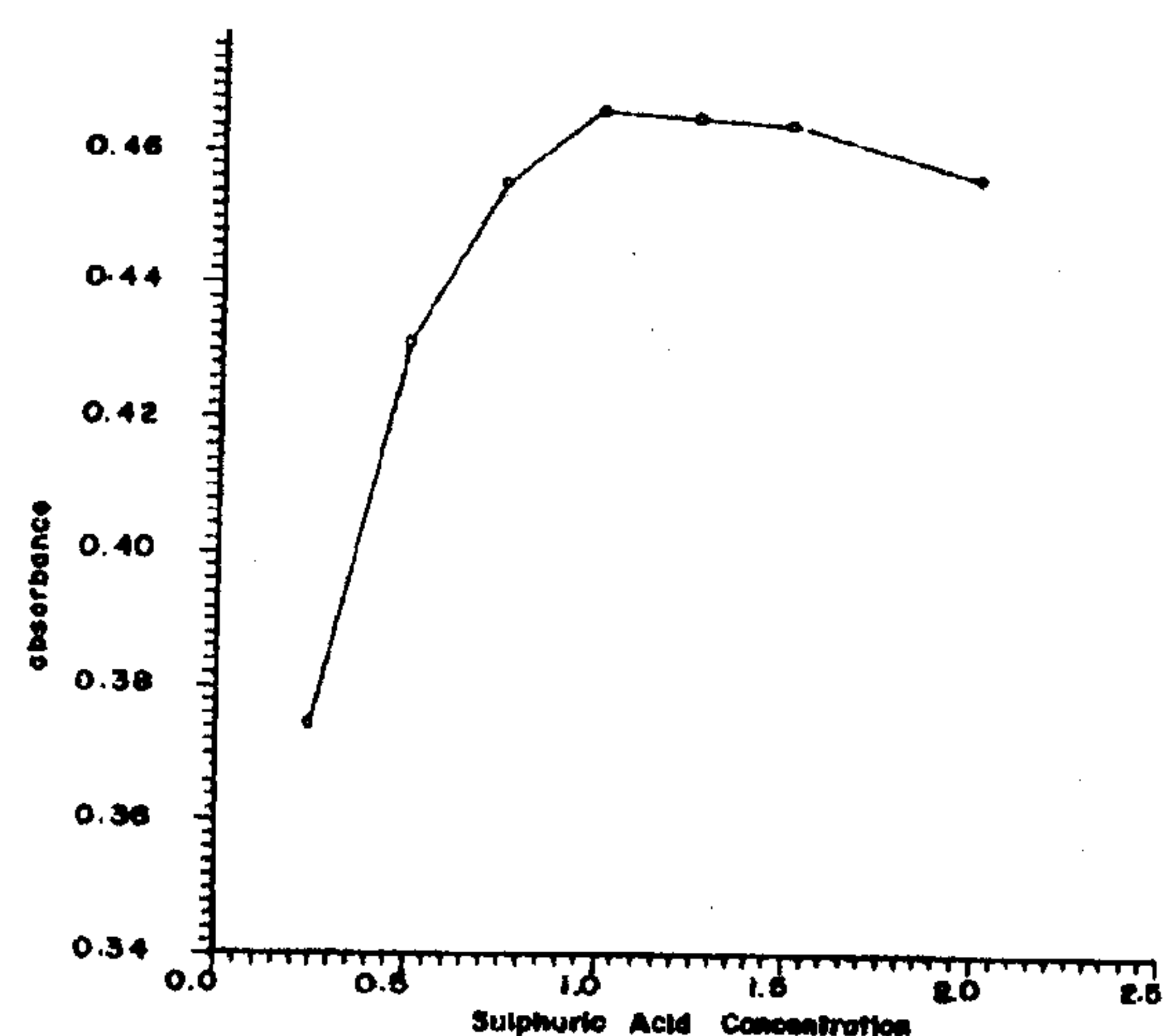


Fig. 3: Effect of variation of sulphuric acid concentration on the absorption intensity of the interaction product of 5 µg/ml N,N-DMPPDA with Na₂S and Fe(III) reagents.

Effect of oxidants concentration

Different concentrations of each oxidant were dissolved in optimum acid concentration and the reaction was carried out in series of 50-ml calibrated flasks containing 5 µg/ml diamine solution and 5 ml sulphide solution (0.015% for PPDA and 0.01% for both N,N DMPPDA and N,N DEPPDA). Figure 4 shows that the optimum concentration of Fe(III) for maximum color development was 0.8% in 0.15 M H₂SO₄ for both PPDA, and N,N DEPPDA, and 0.6% in 1 M H₂SO₄ for N,N DMPPDA. Similarly, other oxidants concentration effect was tested.

Effect of temperature and the reaction time

Optimum reaction time was determined by following the color development of the reaction products of diamines with sodium sulphide and an oxidant at room temperature and in thermostatically controlled water bath at different temperatures. The flasks were removed at different periods ranging from 5-50 minutes,

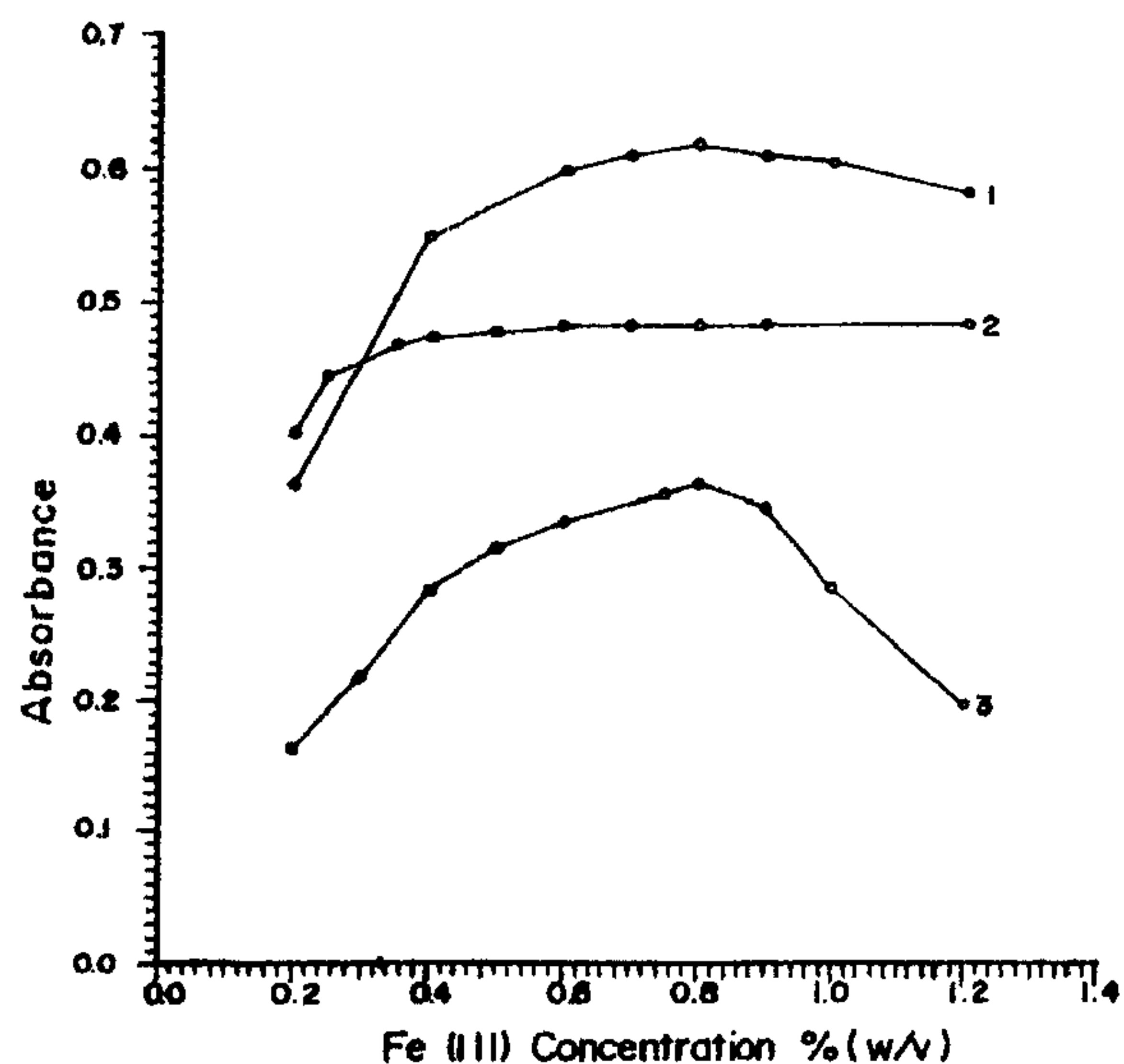


Fig. 4: Effect of variation of Fe(III) concentration on the absorption intensity of the reaction product of 5 $\mu\text{g/ml}$: 1) PPDA, 2) N,N-DMPPDA and 3) N-DEPPDA, with Na_2S and Fe(III) reagents.

then cooled and diluted to the volume. The absorbances were measured against a reagent blank treated similarly. It was found that the reaction is very rapid at higher temperature, reached maximum within few seconds. However, the color fades rapidly with time, most probably due to loss of H_2S at higher temperature. While at room temperature the

color increased gradually and reached maximum after five minutes. Hence this reaction time at room temperature is recommended all over the work.

Effect of solvent variation

Dilution of the colored reaction product by different solvents showed no effect on λ_{max} while absorption intensity is influenced slightly. The obtained data using Fe(III) as oxidant are shown in Table 3. Any of the polar solvents listed in Table 3 could be used for the dilution of the reaction product. However, distilled water was used throughout this study.

Color stability

After dilution of the colored solution with distilled water, a gradual increase in absorption intensity was observed throughout the first 10 minutes and then remained constant for >24 hours. Therefore standing time of 10 minutes is recommended.

Order of reagents addition

The order of reagents addition was very important as the sulphide solution had to be added to the sample and finally the oxidant. Changing the order of addition produced low results in case of Fe(III) and Ce(IV) and produced no color in case of N-bromosuccinimide.

Table 3: Effect of diluting solvents on the absorption intensity for the reactions product of 5 $\mu\text{g/ml}$ diamine with sodium and Fe(III) reagents.

Solvent	PPDA		N,N-DMPPDA		N,N-DEPPDA	
	λ_{max}	A^*	λ_{max}	A^*	λ_{max}	A^*
Distilled water	597.2	0.595	665.0	0.440	670.0	0.380
Isopropanol	603.2	0.640	659.9	0.490	665.4	0.376
Ethanol	602.2	0.650	608.6	0.494	665.4	0.450
Methanol	598.2	0.635	656.4	0.490	663.6	0.410
DMSO	606.8	0.563	659.0	0.450	672.0	0.373
Dioxane	603.1	0.631	659.9	0.484	603.1	0.402

* Average of three determinations.

Quantification

Under the proposed experimental conditions, linear response between the absorbance and concentration was observed over the concentration ranges given in Table 4 (a,b and c), correlation coefficient, intercept and calibration data are listed in the table.

Specificity

o-Phenylenediamines, monosubstituted aromatic amines and aliphatic amines produced completely different colors under the described experimental conditions most probably due to oxidation of the diamine. Thus, the method could be considered selective for *p*-phenylenediamines.

Table 4a: Comparative summary of some statistical data, for diamines analyzed by sodium sulphide and Fe(III) reagents.

Compound	Concentration range ($\mu\text{g/ml}$)	Slope	Intercept	(r)
PPDA	1-10	0.11	-0.020	0.9999
N,N-DMPPDA	1-9	0.09	0.002	0.9998
N,N-DEPPDA	1-10	0.08	-0.050	0.9999

Table 4b: Comparative summary of some statistical data, for diamines analyzed by sodium sulphide and cerium(IV) reagents.

Compound	Concentration range ($\mu\text{g/ml}$)	Slope	Intercept	(r)
PPDA	1-7	0.05	-0.031	0.9999
N,N-DMPPDA	2-7	0.04	-0.018	0.9999
N,N-DEPPDA	2-7	0.04	-0.038	0.9994

Table 4c: Comparative summary of some statistical data, for diamines analyzed by sodium sulphide and NBS reagents.

Compound	Concentration range ($\mu\text{g/ml}$)	Slope	Intercept	(r)
PPDA	2-8	0.038	0.011	0.9716
N,N-DMPPDA	2-8	0.033	0.050	0.9963
N,N-DEPPDA	2-8	0.017	-0.015	0.9750

Determination of *p*-phenylenediamines in spiked water samples

Water from River Nile was first tested for aromatic diamines. The water was found to be free from aromatic diamines. Hence, synthetic samples, were prepared by adding known amounts of N,N DMPPDA and analyzing these samples by the proposed method using the standard addition technique. Excellent recoveries were obtained confirming the validity of the proposed method for the determination of aromatic diamines in polluted water; the results are shown in Table 5.

Investigation of reaction mechanism

The reaction product of N,N DMPPDA with Fe(III) and sodium sulphide could be isolated as picrate or perchlorate salt and subjected to TLC, UV-Vis and IR identification tests. The absorption spectrum of the isolated product in methanol shows a single peak at 652 nm which is identical with that of perchlorate salt of methylene blue authentic sample. In addition the IR spectra of both perchlorate and picrate salts of the isolated products compared with those of methylene blue authentic are shown in Figure 5. From the microanalysis data, UV and IR spectra a mechanism of the reaction could be suggested (Scheme 1).

Table 5: Determination of diamines in spiked water sample using sodium sulphide and Fe(III) reagents.

S. No.	Added ($\mu\text{g/ml}$)	PPDA %Recovery \pm S.D.	N,N-DMPPDA %Recovery \pm S.D.	N,N-DEPPDA %Recovery \pm S.D.
1	3	96.67 \pm 0.9	101.60 \pm 0.7	96.33 \pm 0.7
2	4	99.87 \pm 0.5	101.50 \pm 0.7	97.56 \pm 0.5
3	6	100.14 \pm 1.5	100.73 \pm 0.8	100.33 \pm 0.8
4	7	101.14 \pm 0.9	98.14 \pm 0.8	100.57 \pm 0.8
5	8	102.00 \pm 0.8	96.03 \pm 0.7	101.12 \pm 0.9

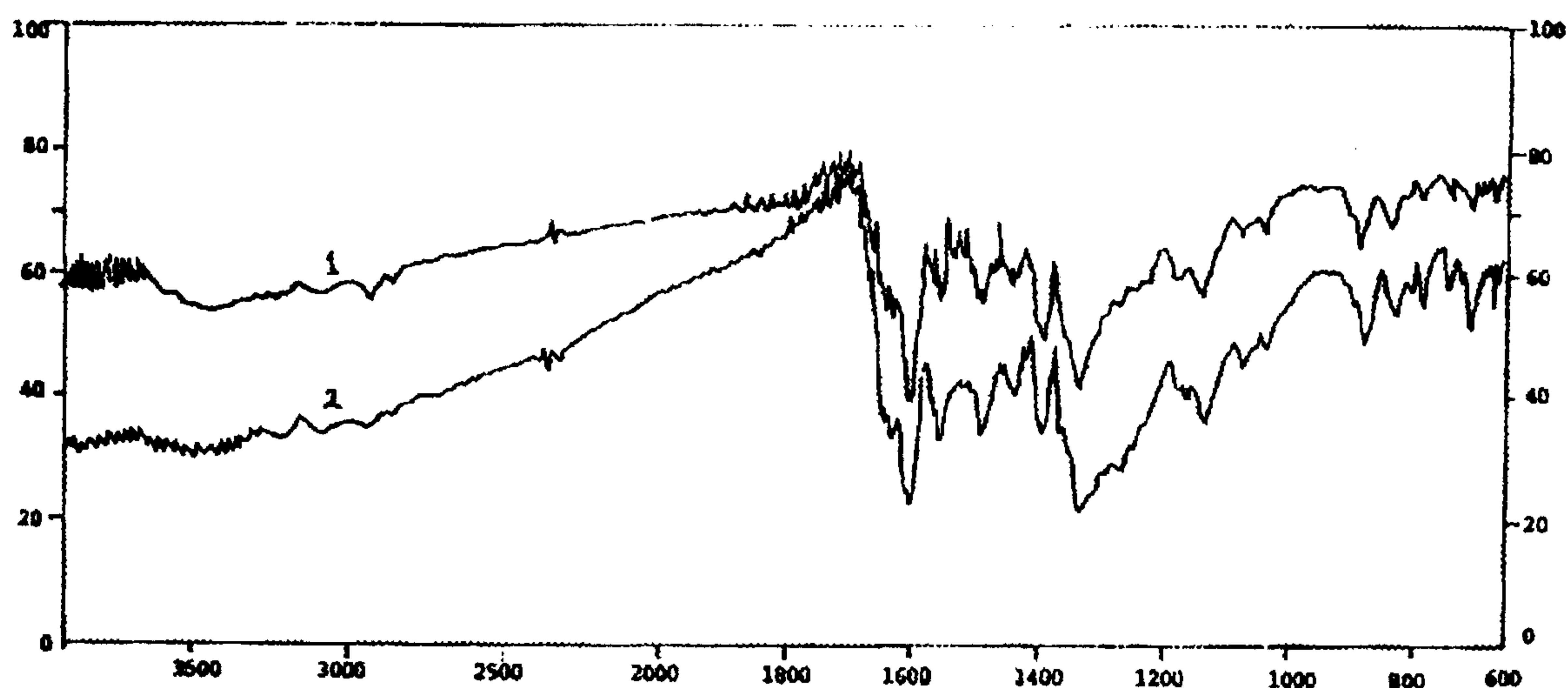
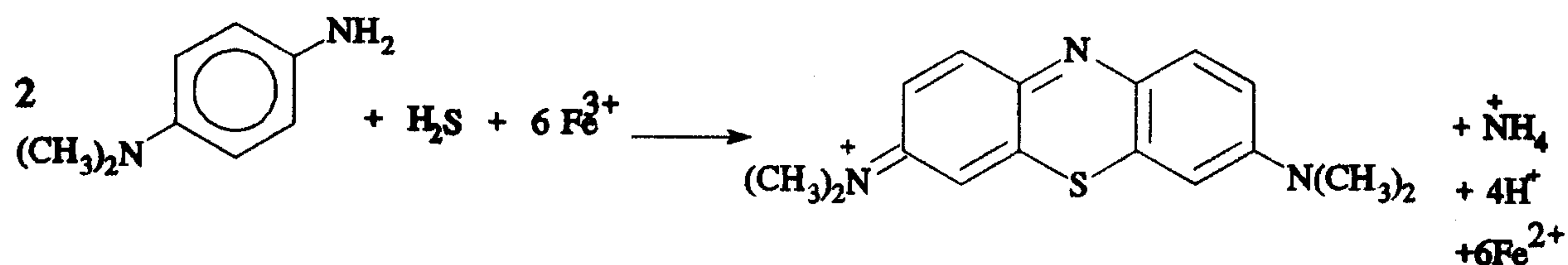


Fig. 5: IR spectra of picrate salt of 1) MB authentic sample and 2) that resulting from the reaction of N,N-DMPPDA with Na₂S and Fe(III) reagents.



Scheme 1

REFERENCES

- 1- The "Merck Index" 12thed., Merck and Co., Inc. USA, p. 550 (1996).
- 2- M. A. Abdalla, A. G. Fogg and C. Burgess, *Analyst*, **107**, 213 (1982).
- 3- G. Choudhary, *J. Chromatogr.* **193**, 277 (1980).
- 4- V. C. Kidwell, "Determination of p-phenylene diamines and its metabolites by liquid chromatography and electrochemistry", Ph.D. Thesis, Purdue University, U.S.A. (1988).
- 5- M. F. M. El-Ghandour and A. Abdel Razeq, *Microchem. J.* **30**, 201 (1984).
- 6- S. T. Sulaiman, L. M. N. Saleem and I. J. El-Nuri, *Microchem. J.*, **29**, 228 (1984).
- 7- S. Koch, G. Ackermann and P. Lindner, *Z. Chem.*, **30**, 74 (1990) through *Anal. Abstr.* **53**, 5D 110 (1991).
- 8- G. Hoogewijs and D. L. Massart, *J. Pharm. Belg.*, **38**, 76 (1983).
- 9- M. Dalene, G. Skarping and H. Tinnerberg, *Chromatographia*, **38**, 776 (1994).
- 10- U. Bachrach and Y. M. Plesser, *Anal. Biochem.*, **152**, 423 (1986).