Differential-pulse Polarographic Micro-determination of Amines *via in situ* Generation of Dithiocarbamates

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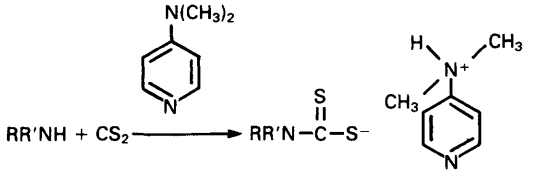
Primary and secondary amines, after *in situ* derivatization to their corresponding dithiocarbamates salts by a two-phase reaction, were determined in aqueous solution using differential-pulse polarography. A single differential-pulse polarographic peak was obtained for dithiocarbamate derived from a secondary amine, whereas dithiocarbamate generated from a primary amine exhibited two peaks in its polarogram. The calibration graphs obtained from all polarographic peaks of the six amines under study were rectilinear over the range 5×10^{-6}–2.5×10^{-5} mol dm^{-3} in the sample solution. For the micro-determination of amines, the method was found to be precise and the detection limit was 20 μg of amine.

Keywords: *Amine; micro-determination; differential-pulse polarography; organic analysis;* in situ *dithiocarbamate generation*

The polarographic determination of organic species has emerged as an important analytical method.[1,2] To extend the scope of application, many electro-inert organic substances, after conversion into their electroactive derivatives, are amenable to polarographic analysis.[3] However, quantitative organic derivatization reactions, especially in micro-scale amounts, are seldom found, which impedes the use of this strategy in the polarographic determination of organic species. Amines represent an important class of organic compounds that is resistant to electroreduction. Previously a spectrophotometric method was reported for the determination of amines *via in situ* generation of the corresponding dithiocarbamate salt.[4] On the other hand, polarographic studies of monoalkyl- and dialkyldithiocarbamates have been well documented.[5,6] In addition, formation of dithiocarbamates and their use in the indirect polarographic determination of amino acids and carbon disulfide have also been reported.[7–9]

As an application of these findings, this paper describes the development of a sensitive polarographic method for the determination of primary and secondary amines *via in situ* generation of their polarographically active derivatives, *viz.*,



Polarographically inactive Polarographically active

Under aqueous conditions, both primary and secondary amines can be quantitatively converted into water-soluble and electroactive dithiocarbamate salts, thereby providing a simple means for their determination.

Experimental

Apparatus

Differential-pulse polarograph (DPP) measurements were carried out by means of a Metrohm (Herisau, Switzerland) E-506 polarograph coupled with an E-505 polarographic stand. A three-electrode combination was used, consisting of a saturated calomel electrode (SCE) as the reference and platinum as the counter electrode. A metrohm Model EA-87620 cell, flushed with high-purity nitrogen, was used throughout. A pulse amplitude of 48 mV was used, with a scan rate of 2.50 mV s^{-1}, a drop time of 2 s and a mercury head of 45 cm.

Reagents

All chemicals were of analytical-reagent grade. Britton-Robinson (BR) buffer solutions, which contained sodium hydroxide and orthophosphoric, glacial acetic and boric acids (pH 8.0–11.5), were all prepared with distilled water (DW) and were used as the background electrolyte.[10]

In situ Derivatization of Amines

For the micro-derivatization reaction, standard solutions of amine and 4-dimethylaminopyridine were prepared separately by dissolving accurately approximately 0.1 g of pure substance in DW in a 100 cm^3 calibrated flask. The standard amine solution (0.2 cm^3), 1 cm^3 of standard 4-dimethylaminopyridine solution and 0.8 cm^3 of DW were mixed together in a 10 cm^3 round-bottomed flask and 1 cm^3 of carbon disulfide was introduced. The two-phase mixture was then stirred at room temperature for 30 min to effect formation of the dithiocarbamate salt and 10 cm^3 of DW were added. The whole mixture was swirled vigorously for 20 s and allowed to settle into two layers, then 2 cm^3 of the upper aqueous layer were pipetted into a 100 cm^3 calibrated flask and diluted to the mark with BR buffer solution at the appropriate pH. The solution was then ready for polarographic analysis.

Determination of Dithiocarbamate by DPP

The dithiocarbamate in 25 cm^3 of BR buffer solution at pH 8.50 (or 10.38) was placed in the cell of the polarograph and flushed with oxygen-free nitrogen for 7 min. The cell was attached to the three-electrode assembly and a flow of nitrogen was maintained over the solution. A potential scan was then performed over the range from 0 to −0.8 V *versus* SCE at a rate of 2.5 mV s^{-1} to obtain a differential-pulse polarogram.

Calibration Graphs for the Micro-determination of Amines

Standard solutions containing different amounts of pure amine (0.2, 0.4, 0.6, 0.8 and 1.0 mg) were derivatized under the described conditions. The resulting solutions, after appropriate dilution with DW in a calibrated flask as described above, were subjected to polarographic analysis. The peak current for each of the derivatized amine (*i.e.*, dithiocarba-

Table 1 *In situ* derivatization conditions for different amounts of diethylamine

Mass of diethylamine/mg	Concentration of amine in the derivatization/mg cm^{-3}	Volume of CS_2/cm^3	Mass of 4-dimethylaminopyridine used/mg	Conversion (%)
2–10	1–5	1.0	50	>96
0.2–1.0	0.1–0.5	1.0	5	>95
0.02–0.1	0.01–0.05	1.0	0.5*	>95

* A 1.0 cm^3 aliquot of aqueous standard 4-dimethylaminopyridine was used for the derivatization reaction.

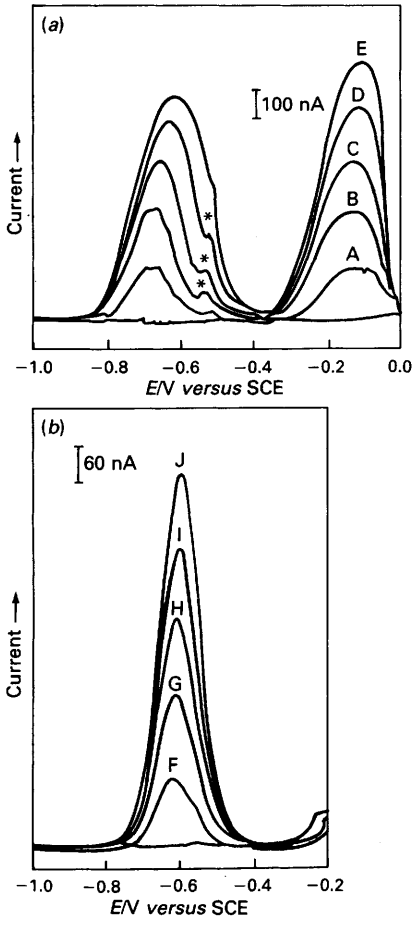


Fig. 1 Typical DPP responses of dithiocarbamates generated *in situ* from 0.1–1 mg of: (*a*) butylamine and (*b*) diethylamine. After appropriate dilution, concentration of the solutions: A, 4.961 × 10^{-6}; B, 9.945 × 10^{-6}; C, 1.491 × 10^{-5}; D, 1.990 × 10^{-5}; E, 2.486 × 10^{-5}; F, 5.036 × 10^{-6}; G, 1.006 × 10^{-5}; H, 1.509 × 10^{-5}; and J, 2.515 × 10^{-5} mol dm^{-3}. Asterisks indicate polarographic peaks due to trithiocarbonate

mate) samples was plotted as a function of amine concentration.

Results and Discussion

In situ Derivatization Reaction

For large-scale reactions (0.1–1 g), in the presence of carbon disulfide and aqueous sodium hydroxide, the conversion of amines into dithiocarbamates was shown to be facile and quantitative by using the ultraviolet spectrophotometric method. However, substantial trithiocarbonate, which is also an electroactive species, was generated under these reaction conditions.[4] For the present investigation, we were particularly interested in extending the derivatization to the microscale and in finding alternative reaction conditions, such that the formation of trithiocarbonate could be minimized if not completely eliminated. Because of the availability of an authentic sodium diethyldithiocarbamate salt, diethylamine was chosen as the representative example for detailed studies. After some experimentation, almost quantitative derivatization of diethylamine into diethyldithiocarbamate was achieved within 30 min under the specified conditions (Table 1). The derivatization was satisfactory for analytical work even for diethylamine concentrations as low as 0.01% (or 0.02 mg absolute amount). Also, it was found that the formation of the interfering trithiocarbonate species could be largely suppressed by use of 4-dimethylaminopyridine as the base. Except for the determination of extremely small amounts of amine (below 0.02 mg), the interfering effect of trithiocarbonate was eliminated.

Characteristics of the DPP Wave

In the presence of carbon disulfide and a base, both primary and secondary amines undergo facile conversion into their corresponding dithiocarbamate salts. The aim of this work was to develop a polarographic method for the determination of both primary and secondary amines. In order to define the scope and limitations of the methodology, the characteristics of the DPP waves for butyl- and diethyldithiocarbamates, derived *in situ* from their corresponding amines, had to be scrutinized. Under the derivatization conditions for diethylamine, a well-defined DPP peak was obtained at −0.61 V *versus* SCE (for a concentration of 1 × 10^{-5} mol dm^{-3} amine). In contrast, for butylamine, two DPP peaks were obtained at −0.67 and −0.15 V *versus* SCE (for a concentration of 1 × 10^{-5} mol dm^{-3} amine). Typical differential-pulse polarograms for the derivatized amines at different concentrations are shown in Fig. 1. In fact, rectilinear working calibration graphs for these two representative amines, covering a wide range of derivatization reactions (20 μg–10 mg), could be obtained (Tables 2 and 3).

Stability of Dithiocarbamate and Trithiocarbonate

Dithiocarbamates are known to be stable under alkaline conditions and decompose readily under acidic conditions. Careful stability-monitoring studies demonstrated that the polarographic peak height of diethyldithiocarbamate solutions reduced at a rate of 1.5% h^{-1} at pH 8.0. However, at pH levels above 8.5, the peak current of the solution after standing for 2 h in the dark remained unchanged, indicating that dithiocarbamates are stable at pH levels above 8.5.

Effect of pH

According to the stability studies, it appears that it is imperative to keep the dithiocarbamate, after its formation from an amine, at a sufficiently high pH to prevent decomposition. However, substantial carbon trithiocarbonate can be generated from the residual carbon disulfide in the alkaline medium during the storage prior to polarographic measurements. In addition, the potential interference effect of trithiocarbonate became more manifest when the concentration of the analyte was low. In particular, more trithiocarbonate will be formed in the derivatization reaction of a primary amine [Fig. 1(*a*)]. In order to ascertain the working pH for the determination of amines, the effect of pH on the peak potential (E_p) values of the DPP waves exhibited by butyldithiocarbamate, diethyldithiocarbamate and trithiocarbonate generated in the *in situ* derivatization reaction was studied. The results are shown in Fig. 2. The E_p of trithiocarbonate, the interfering species, which is pH dependent, shifts to more negative values as the pH increases, whereas the E_p of diethyldithiocarbamate appears to be constant over the range

Table 2 Working calibration graph data for the micro-determination of diethylamine

Milligram level			Sub-milligram level			Microgram level		
Mass of sample/mg	Concentration of the solution* after dilution/mol dm^{-3}	i_p/nA	Mass of sample/mg	Concentration of the solution† after dilution/mol dm^{-3}	i_p/nA	Mass of sample/mg	Concentration of the solution‡ after dilution/mol dm^{-3}	i_p/nA
1.968	6.416×10^{-6}	150	0.202	5.036×10^{-6}	114	20.4	2.540×10^{-6}	68
3.936	1.283×10^{-5}	300	0.405	1.006×10^{-5}	226	40.8	5.081×10^{-6}	125
5.904	1.925×10^{-5}	450	0.607	1.509×10^{-5}	336	61.2	7.620×10^{-6}	185
7.872	2.566×10^{-5}	618	0.810	2.012×10^{-5}	456	101.6	1.016×10^{-5}	245
9.840	3.208×10^{-5}	786	1.010	2.515×10^{-4}	570	127.0	1.270×10^{-5}	293
$r = 0.9996$			$r = 0.9999$			$r = 0.9993$		

* Dilution factor = 2.38×10^{-4}.
† Dilution factor = 1.82×10^{-3}.
‡ Dilution factor = 9.09×10^{-3}.

Table 3 Working calibration graph data for the micro-determination of butylamine

Milligram level				Sub-milligram level			
Mass of sample/mg	Concentration of the solution* after dilution/mol dm^{-3}	i_p/nA Peak 1	i_p/nA Peak 2	Mass of sample/mg	Concentration of the solution† after dilution/mol dm^{-3}	i_p/nA Peak 1	i_p/nA Peak 2
2.020	6.586×10^{-6}	162	156	0.199	4.960×10^{-6}	170	160
4.040	1.317×10^{-6}	330	312	0.399	9.945×10^{-6}	310	320
6.060	1.976×10^{-5}	486	486	0.598	1.491×10^{-5}	450	460
8.080	2.634×10^{-5}	630	600	0.798	1.990×10^{-5}	580	580
10.100	3.293×10^{-5}	780	684	0.997	2.486×10^{-5}	710	650
		$r = 0.9996$	$r = 0.9913$			$r = 0.9998$	$r = 0.9906$

* Dilution factor = 2.38×10^{-4}.
† Dilution factor = 1.82×10^{-3}.

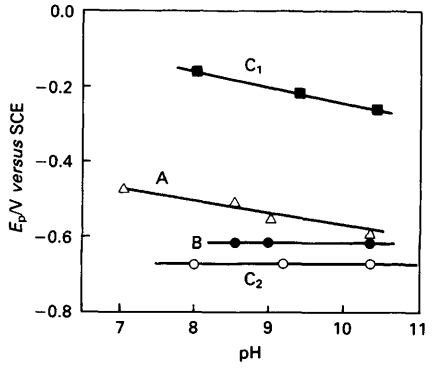


Fig. 2 E_p *versus* pH for the DPP wave exhibited by: A, trithiocarbonate; B, diethyldithiocarbamate; and C_1 and C_2, butyldithiocarbamate (two peaks)

of pH studied. The two polarographic peaks for butyldithiocarbamate respond differently to pH change. As the pH changed, the more negative E_p of its polarogram (*i.e.*, −0.67 V) remained unchanged while a considerable shift in the more positive E_p (*i.e.*, −0.15 V) was observed.

In summary, the stability and pH studies enabled the optimum pH for the reactions to be selected. For primary amines, the formation of trithiocarbonate is fairly serious; it is advisable that the polarographic measurement is carried out at pH 8.5. Although both the peaks are suitable for analytical work, the less negative peak (E_p = −0.15 V), which is free from trithiocarbonate interference, was used. At low concentrations of butylamine, the less negative peak shifted sufficiently close to 0 V to result in great distortion of the polarographic wave. Hence, the peak at −0.67 V was used for the determination of sub-milligram levels of primary amine.

Determination of Other Amines

In order to demonstrate the scope of application of the method, four additional amines, *viz.*, propylamine, hexylamine, pyrollidine and morpholine, were subjected to polarographic studies. The polarogram for the dithiocarbamates derived from the two primary amines exhibited two peaks, whereas that for the two secondary amines displayed only one peak, reminiscent of butylamine and diethylamine, respectively. Each peak was characterized by its own E_p, and all the peak heights were rectilinearly related to amine concentration and were therefore suitable for quantitative analysis.

Table 4 Micro-determination of amines *via in situ* derivatization to the corresponding dithiocarbamates

Entry	Amine	Mass of amine used/mg	Mass of amine* found/mg	Error (%)
1	Butylamine	7.158	7.278	+1.3
2		5.132	5.252	+2.3
3		0.748	0.792	+5.9
4		0.534	0.565	+5.8
5		0.0801	0.0840†	+5.0
6		0.0342	0.0342†	0.0
7		0.0229	0.0216†	−5.6
8	Propylamine	0.719	0.720	+0.1
9		0.514	0.520	+1.2
10	Hexylamine	0.830	0.855	+3.0
11		0.593	0.618	+4.2
12	Diethylamine	6.390	6.131	−4.0
13		4.564	4.408	−3.4
14		0.708	0.679	−4.1
15		0.506	0.481	−5.0
16		0.0710	0.0729	+2.7
17		0.0510	0.0505	−1.0
18	Pyrollidine	0.809	0.828	+2.3
19		0.578	0.584	+1.0
20	Morpholine	0.815	0.838	+2.8
21		0.582	0.611	+5.0

* Average of three determinations, deduced from working calibration graphs.
† Determined by direct-comparison method with standards.

Viability of the Method for the Micro-determination of Amines

For the actual determination of amines, in milligram and sub-milligram samples, quantitative results could be obtained by using the working calibration graphs covering the appropriate amounts of standards. For primary amine samples, on the microgram scale (*i.e.*, entries 5–7 in Table 4), a direct comparison with dithiocarbamate standards, derived from butylamine, was used. The errors for all determinations of six amines, covering a broad range of sample sizes, were found to be within ±6%.

Conclusion

A general, indirect polarographic method for the determination of primary and secondary amines has been developed. The method can be carried out in aqueous solution and can be used to detect as little as 20 μg of amines with great accuracy and precision.

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Paper 2/03537E
Received July 6, 1992
Accepted August 10, 1992