

# Determination of aliphatic amines in mineral flotation liquors and reagents by high-performance liquid chromatography after derivatization with 4-chloro-7-nitrobenzofurazan<sup>☆</sup>

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## Abstract

The method described here fulfils the need for a suitable analytical method to determine the concentrations of single and mixed aliphatic amines in the range from hexylamine (C<sub>6</sub>) to octadecylamine (C<sub>18</sub>) in flotation test solutions and in commercial flotation collectors. Amines do not have a UV–vis spectrum in aqueous solution but by reacting an amine-containing solution with 4-chloro-7-nitrobenzofurazan solution (chloro-NBD), derivatized products (amino-NBDs) are formed which have absorbance maxima at 470 nm. Excess chloro-NBD and the amino-NBDs can be separated from each other by high-performance liquid chromatography (HPLC) and their concentrations measured with a UV–vis detector. Important variables in the derivatization stage are pH, temperature, chloro-NBD concentration, and reaction time, all of which interact with each other. A three-stage statistical procedure was used to determine the optimum conditions. In each stage, an 8-test design was used in which a high and low limit was set for each variable, and the chromatogram peak area of the derived amino-NBD was measured. The optimum derivatization conditions established were pH 8.9, chloro-NBD concentration 0.20% (w/v), temperature 70 °C, and reaction time 60 min. Optimum elution conditions for chromatography were an eluent containing 80% (v/v) acetonitrile in aqueous solution containing 40 mM acetic acid at pH 4.5. With a flow rate of 2.0 ml/min, dodecylamine had a retention time of about 3 min, whereas octadecylamine had a retention time of 44 min. Straight-line calibration curves were obtained up to at least 200 ppm of amine in solution. The lower limit of detection was estimated to be 0.05 μM (10 ppb) with a signal to noise ratio of 3. No interfering substances were found. The method was successfully applied to the analysis of solutions from an actual flotation test and to a solid commercial amine.

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## 1. Introduction

Alkyl amines are commonly used as collectors in non-sulphide mineral flotation systems. One example of this is the separation of chromite and chrome spinels from ilmenite concentrates. In this system, amines or amine acetates are

added to float the chromite in the presence of sodium fluoride as an activator for the chromite, and starch as a depressant for the ilmenite, at a selected pH adjusted by additions of acid or alkali. The amines are added on an empirical basis, because no reliable analytical method is available for the determination of the concentration of the amines in the flotation solution. The development of the method described here should facilitate the optimization of amine additions in such a system.

Furthermore, since the amines commercially available for flotation are mainly manufactured from natural products, they commonly contain several alkyl amines with different carbon

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chain lengths (C<sub>6</sub>–C<sub>18</sub>), and it would be helpful if the proportions of the different amines in solution could be quantified. In addition, it would be valuable if the method selected could be readily adapted to determination of the amines in the original reagent. The amine reagents, in pure or commercial form, are available in liquid or solid form, depending on the carbon chain length, as either amines or as amino acetates.

Many collectors and other reagents used in sulphide mineral flotation systems can be determined by UV absorption directly on an aqueous solution or after extraction into an organic solvent or after conversion to a metal complex dissolved in an organic solvent, as discussed by Jones and Woodcock [1]. However, the amines under consideration here have no UV or visible absorption spectra and another method is required. Early reviews of amine determinations by Wang et al. [2] and Tsubouchi [3] discussed non-specific methods, which were not of value for the present purpose or had various disadvantages, such as not being applicable in saline water, which may be used in flotation.

Kostyukovskii et al. [4] investigated the determination of micro amounts of *N*-nitrosoamines in water and foodstuffs. They used HBr to denitrosate the *N*-nitrosoamines, and then used chloro-NBD to prepare the derivatives for examination. They then used various methods to determine the concentration of the original amine, but these methods did not distinguish between different alkyl amines and were therefore not appropriate for this work.

Sahasrabuddhey et al. [5] developed a method for determining ammonia and a number of aliphatic amines in environmental waters. This method involved the pre-column conversion of the amines into phenylthiourea or its derivatives by reaction with phenyl isothiocyanate. Only ammonia and short chain amines (C<sub>1</sub>–C<sub>4</sub>) were examined and it was not clear whether or not the method was applicable to longer chain amines present in flotation systems

Khryashchevskii et al. [6] developed a method for the determination of amines in flotation collectors used for the flotation of potassium salts. They used chloro-NBD to produce derivatives of the amines present [that is, higher primary aliphatic amines (C<sub>10</sub>–C<sub>20</sub>)], separated them by high-performance liquid chromatography (HPLC), and measured the absorbance at 460 nm to determine the amine concentration. However, they used methyl isobutyl ketone (MIBK) for an extraction procedure in their work; this was not practical for the present purpose. Nevertheless, an adaptation of the method seemed to be suitable for measurement of the concentrations of amines in flotation pulps and was therefore chosen for examination in this work.

Subsequent to the development of the method described here, Verdú-Andrés et al. [7] published a method for determining low levels of short chain amines, e.g. ethyl amine and dimethyl amine, in environmental water samples. Their method involved pre-concentration of the amines on solid-phase extraction cartridges. This was not applicable for lab-

oratory flotation tests as a maximum sample volume of only about 10 ml at a time can afford to be taken from a laboratory flotation cell.

None of the above methods was directly applicable to flotation solutions. The method selected for investigation was one involving the formation of a derivative of each amine present by heating the aqueous solution with 4-chloro-7-nitrobenzofurazan, which is sometimes called 7-chloro-4-nitrobenzene-2-oxa-1,3-diazole (termed chloro-NBD here), separating the derivatized amino-NBD products from excess chloro-NBD and each other by HPLC, and measuring the concentration of each product by UV–vis spectroscopy.

## 2. Experimental

Pre-column derivatization was selected for study, and the main variables, namely derivatization temperature, pH, chloro-NBD concentration, and reaction time, were examined. Because these variables interacted with each other, a three-stage statistical evaluation was undertaken, using a series of 8-experiment runs (after Taguchi and Wu [8]), as discussed later, to optimise the conditions. Optimum conditions for HPLC elution were then investigated. Finally, the method was applied to solutions from an actual batch flotation test and to a sample of coco amine acetate, which was available in our laboratory.

### 2.1. Major equipment and instrumentation

A Varian (Palo Alto, USA) Cary 500 UV–vis spectrophotometer was used to check the absorbance spectra of aqueous solutions of the chloro-NBD and amino-NBD derivatives. Measurements were made in 1.0 cm cells against a reference of Milli-Q water.

Chromatographic analyses were carried out with a Hewlett-Packard (Palo Alto, USA) HP 1100 series unit incorporating a module G1312A binary pump and a G1315A diode array detection (DAD) system. Sample solutions were injected into the system with a Gilson (Middleton, USA) 233XL auto-sampler, and separated on a Waters (Milford, USA) Nova-Pak C<sub>18</sub> column (150 mm long by 3.9 mm i.d.). Chromatograms and spectral data were collected and processed with Hewlett-Packard Chemstation software.

### 2.2. Ancillary equipment

Pre-column derivatization of the samples at temperatures up to 75 °C was conducted in 4 ml vials in a temperature-controlled aluminium block. The block was maintained at the desired temperature by pumping water from a Grant (Shrepreth, UK) thermostated water bath LTD6/G through internal channels in the block.

### 2.3. Reagents and solutions

Reagent grade *n*-hexylamine, *n*-octylamine, *n*-decylamine, *n*-dodecylamine, *n*-tetradecylamine, and *n*-octadecylamine were all obtained from Sigma–Aldrich (St. Louis, Mo, USA). A commercial amine flotation collector, made by Armour Industrial Chemical Co. (Chicago, USA) was used in some of the work. Stock solutions of these amines containing  $1.00 \times 10^{-2}$  mol/l were prepared individually in methanol, as they are relatively insoluble in water, and diluted for use as required.

A stock solution containing 0.4 % (w/v) of chloro-NBD (Sigma–Aldrich) was prepared in methanol and used as required.

The final optimized eluent consisted of 80% (v/v) HPLC-grade acetonitrile (BDH, Poole, UK) in water buffered at pH 4.5 with 40 mM acetic acid. This solution was delivered at 2.0 ml/min. However, some experiments were done with a similar solution containing 80% (v/v) methanol in water instead of acetonitrile, some with a solution containing 80% (v/v) tetrahydrofuran, and some with 0.10 M tetrabutyl ammonium acetate (TBA) in water.

All other chemicals were obtained as analytical-reagent grade and used without further purification. All water used in the experiments was double distilled and then passed through a Millipore (Bedford, MA, USA) purification system.

### 2.4. Laboratory flotation test

A laboratory flotation test was conducted on a typical ilmenite–chromite–quartz mineral sand mixture using base line conditions as detailed later. Reagents used were hexylamine and dodecylamine as collectors, starch as a depressant, and sodium fluoride as an activator. Solution samples (about 10 ml) were taken at pre-determined times and filtered through 1.2  $\mu$ m aperture Millipore filters to provide clear solutions for determination of the two amines present in solution.

## 3. Results and discussion

Results discussed here include those of preliminary work, details of pre-column investigations of important variables and statistical optimization of the major factors, selection of chromatography conditions, and the application of the preferred method to solutions from a flotation test and to a coco amine flotation collector.

### 3.1. Preliminary investigations

A preliminary investigation confirmed that the UV–vis spectrum of the derivatized product had two absorbance maxima (345 nm and 470 nm) and that 470 nm was suitable for subsequent HPLC measurements.

The basic derivatization reaction in aqueous solution, in which the chlorine atom in the chloro-NBD is replaced by an amine group to give an amino-NBD with the co-formation of HCl, is shown in Fig. 1.

Preliminary experiments also confirmed that HPLC could separate the derivatized amines from each other and from excess chloro-NBD.

### 3.2. Derivatization

The main factors affecting the pre-column derivatization of an amine with chloro-NBD (reaction time, temperature, pH, and chloro-NBD concentration) were examined using a standard injection of 100  $\mu$ l of 0.10 mM dodecylamine solution. Initially, a preliminary statistical optimization of the conditions required for derivatization was conducted using an orthogonal table (after Taguchi and Wu [8]).

This required the selection of two levels (a high and a low level) of each of the above parameters, as shown in Table 1. The design supplied by this table thus provides a balanced array of levels constructed in such a way that the effect of each variable, as well as three of the two-variable interaction effects (pH  $\times$  T, pH  $\times$  [NBD], and T  $\times$  [NBD]), can be separately estimated without disturbance from each other as explained in detail by Taguchi and Wu [8]. The lower level of chloro-NBD was prepared stoichiometrically in the ratio 1:1 with the amine concentration in solution. Other factors were kept constant.

Results of the preliminary investigation are summarized in Table 2 and Fig. 2. In Table 2, the criterion for evaluation was the peak area in the corresponding chromatogram, after conversion of each area to the relative yield, expressed as a percentage of the maximum peak area obtained.

In Table 2 a negative value shows a decrease in yield of the derivatized product whereas a positive value shows an increase in yield. The magnitude of the value indicates the relative magnitude of the change. For example, using stage 1 conditions for a change in pH from 9.5 to 10.5 (Table 1), the result (shown in Table 2) is  $-25.2$ , indicating that pH 9.5 is much better than pH 10.5. Similarly, the effect of reaction time in changing from 20 min to 60 min (Table 1) is  $+24.4$  (Table 2), indicating that an increase in reaction time has a

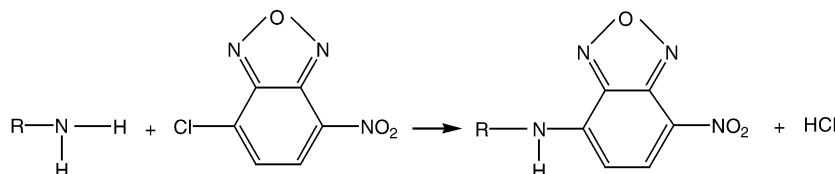


Fig. 1. Chemical reaction of an aliphatic amine with chloro-NBD to give an amino-NBD and HCl. R = Aliphatic alkyl group.

Table 1  
Summary of experimental derivatization conditions for three-stage statistical development of preferred conditions

Stage	Parameter level	pH value	Temperature ( $T$ ) ( $^{\circ}\text{C}$ )	Chloro-NBD concentration (mM)	Reaction time (min)
1	1	9.5	70	0.10	20
	2	10.5	50	0.50	60
2	1	8.5	60	5.0	20
	2	9.0	70	10.0	60
3	1	9.0	60	5.0	40
	2	9.5	70	7.5	70

Table 2  
Results (effects) of three-stage statistical development of preferred derivatization conditions

Stage	pH	$T$	$\text{pH} \times T$	[NBD]	$\text{pH} \times [\text{NBD}]$	$T \times [\text{NBD}]$	Time	Maximum peak area <sup>a</sup>
1	-25.2	-26.8	-10.8	+22.5	+8.7	+10.4	+24.4	245,000
2	-6.2	+11.8	+4.2	+14.0	+4.1	+0.9	+5.8	3289,000
3	-3.2	+5.0	+2.3	+5.2	+2.6	+3.2	+4.9	3421,000

<sup>a</sup> Area under chromatographic peak in arbitrary relative units of milli-absorbance  $\times$  time (mAU s).

large positive effect. As the optimum range is narrowed in stages 2 and 3, the magnitude of the effects is decreased.

### 3.2.1. Reaction time and temperature

Reaction time is important (Fig. 2), but is strongly affected by temperature and pH. Thus at the higher temperature ( $70^{\circ}\text{C}$ ), and pH 9.5, the yield reaches a maximum after about 70 min reaction and then declines. However, at  $70^{\circ}\text{C}$  and pH 10.5, the maximum was reached after about 20 min, but was much lower. In the other two combinations of temperature and pH shown on Fig. 2a maximum was not reached and the peak area values obtained were relatively low (Table 1). This indicates that the reaction is endothermic. Although the yield could possibly be increased further by raising the temperature to an even higher value, this did not seem practicable given the high proportion of acetonitrile present. However, at  $50^{\circ}\text{C}$  the reaction is relatively slow, and as shown on Fig. 2 and in Table 2, relatively long times are required to give a

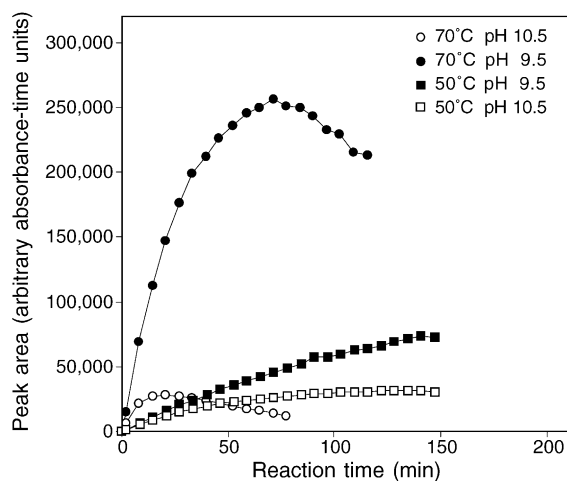


Fig. 2. Effect of reaction time on amino-NBD derivatization using 0.5 mM chloro-NBD solution at two pH levels and two temperatures.

reasonable yield of amino-NBD, so that temperatures above about  $60^{\circ}\text{C}$  are to be preferred.

### 3.2.2. Reaction pH

Results in Table 1 and Fig. 2, discussed above, indicate that the pH of the derivatization solution does have an effect on the reaction. For example, the two curves at  $50^{\circ}\text{C}$  on Fig. 2 show that a lower yield was obtained at pH 10.5 than at pH 9.5. This decrease in yield with increase in pH is unusual, as the derivatization process is a proton-producing reaction. It was therefore decided to also look at a wider pH range (pH 5–13) to check this point.

A 0.1 mM solution of dodecylamine was prepared in 0.10 M solutions of acetic acid (pH 5.2), sodium bicarbonate (pH 8.9), and tetrabutyl ammonium acetate (TBA) (pH 13.3). All three solutions were made up to 10 mM chloro-NBD, reacted at  $70^{\circ}\text{C}$  for 25 min, and then injected into the HPLC system for analysis. The resultant chromatograms showed that at pH 5.2, neither a chloro-NBD peak nor an amino-NBD peak was obtained. At pH 13.3, there was a large solvent peak but no amino-NBD peak. However, at pH 8.9, there was a large solvent peak followed 3.6 min later by an amino-NBD peak. Data from Perrin [9] indicate that a solution of sodium bicarbonate is buffered at about the preferred pH (8.5–8.9) for derivatization and this was therefore used in subsequent work.

### 3.2.3. Chloro-NBD concentration

It was noted above that increasing the chloro-NBD concentration from 0.10 mM to 0.5 mM gave a higher yield of amino-NBD (Table 2). This is typical of an organic reaction with a high reagent ratio pushing the reaction to the product side. Moreover, this was an important finding, and so in the next set of experiments the chloro-NBD concentration was increased still further, i.e., to 5.0 mM and 10 mM, or 50–100 times the concentration of the amine. This ensured that excess chloro-NBD was present so that the amine could

be fully derivatized. In addition, the pH range was restricted to pH 8.5–9.0.

Results presented in Table 2 for the second stage of statistical experiments show that reasonably high yields of amino-NBD were obtained in most experiments, with the highest level being obtained at a pH of 8.5, together with 10 mM of chloro-NBD at 70 °C for a reaction period of 20 min. Further examination of the results in Table 2 shows that there are no other significant changes in the yield of amino-NBD. Changing the pH from 8.5 to 9.0 showed a small negative effect on the derivatization, but a pH of about 9 is most readily achieved by simply adding sodium bicarbonate buffer, and so this level was used in further work.

Apart from temperature and time, which were shown earlier to be important parameters, the most important factor is the chloro-NBD concentration. However, although there is clearly an advantage in increasing the chloro-NBD concentration from 0.50 mM to 5 mM, there is only a 7% increase in yield when the chloro-NBD concentration is increased from 5 mM to 10 mM. The maximum peak area for the second stage statistical experiments was 13-fold greater than for the stage 1 experiments. A small further increase in the yield was obtained in the third stage experiments (Table 2). Even further increases may be possible but this was not examined.

It is interesting to note that the combined effect of chloro-NBD concentration and temperature is lower than either of these factors individually.

### 3.2.4. Final selection of derivatization conditions

Results in Table 2 showed that good results (highest yield of amino-NBD to date) were obtained with a combination of pH 8.5, a reaction temperature of 70 °C, a 70 min reaction time, and a chloro-NBD concentration of 10.0 mM.

After considering the above data and some practical factors, it was decided that the preferred derivatization technique would be to first adjust the pH of the solution to  $8.9 \pm 0.1$  by adding sodium bicarbonate, and to then add sufficient chloro-NBD to give a concentration of at least 0.20% in the solution. This latter figure is very close to 7.5 mM, given that the molecular weight of chloro-NBD is 199.55. The resultant solution should then be derivatized at 70 °C for 60 min.

### 3.2.5. Selection of chromatography conditions

After optimization of the sample preparation conditions, three chromatographic eluents were examined for the separation of the aliphatic amine derivatives. These eluents were (i) 80% (v/v) acetonitrile in water prepared in 40 mM acetic acid with the pH adjusted to 4.5 with dilute sodium hydroxide solution, (ii) 80% (v/v) methanol also prepared in 40 mM acetic acid and the pH adjusted to 4.5, and (iii) 80% (v/v) tetrahydrofuran in water. Acetic acid was used in the eluent to maintain conditions suitable for the silica-based C<sub>18</sub> column.

A mixture of five amines (decylamine, dodecylamine, tetradecylamine, hexadecylamine, and octadecylamine), each at a concentration of 0.02 mM in methanol, was pre-

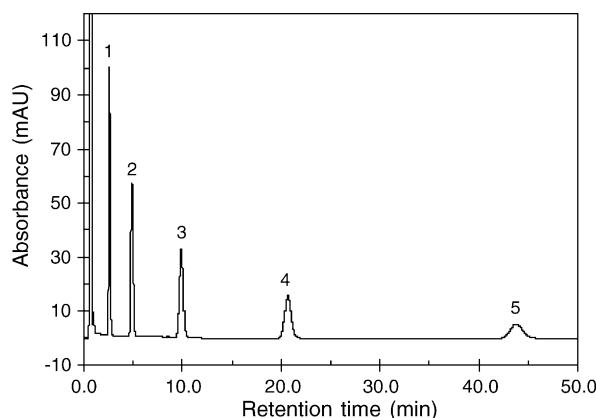


Fig. 3. Chromatogram of a mixture of aliphatic amines using an eluent containing 40 mM sodium acetate in 80% (v/v) acetonitrile delivered at 2.0 ml/min. The derivatized mixture of amino-NBDs injected contained decylamine (peak 1), dodecylamine (peak 2), tetradecylamine (peak 3), hexadecylamine (peak 4), and octadecylamine (peak 5).

pared and derivatized under the optimised conditions developed above. A series of 100  $\mu$ l sub-samples of each solution was injected into the chromatographic system and the chromatograms for each eluent were obtained.

Results for the acetonitrile eluent are given in Fig. 3. This chart shows an unnumbered peak within the first minute of elution representing the unused chloro-NBD. The numbered peaks then represent, in order of increasing carbon chain length (C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, and C<sub>18</sub>), the five amines in the original test solution. A good separation between the five amines was achieved, although the peak height decreased and the retention time increased as the chain length of the amine increased, as expected.

Similar chromatographic results were obtained with the methanol eluent, except for longer retention times for all the amines present. For example, the peak for octadecylamine did not appear until 257 min retention time, compared with 44 min for acetonitrile. Moreover, the peak heights were lower for the methanol eluent than for the acetonitrile eluent. In addition, because the methanol eluent had a relatively high viscosity, which built up a high back-pressure in the column, it had to be delivered at a lower flow rate (1.5 ml/min instead of 2 ml/min), which partly accounted for the longer retention time.

No satisfactory chromatogram was obtained for the tetrahydrofuran eluent as all the amino-NBDs were eluted in the first 2 min without separation. Hence the acetonitrile eluent was selected for future routine analysis.

### 3.2.6. Calibration and detection limit

Typical calibration graphs were obtained by first dissolving separately reagent grade *n*-hexylamine and *n*-dodecylamine in methanol to give  $1.00 \times 10^{-2}$  mol/l stock solutions. These stock solutions were diluted in water as required to give test solutions in the concentration range 0–1 mM (about 0–100 ppm hexylamine and 0–185 ppm dode-



cylamine). Stock solutions containing higher amine concentrations, such as 0.40 mM, could not be completely dissolved in aqueous solution, even when the sample solution contained 50% (v/v) of methanol. The test solutions were then derivatized and separated using the conditions described above.

Results were plotted as peak area versus dodecylamine concentration. The graphs obtained (not given here) showed good linearity between amine concentrations and peak areas over the concentration range from 0.0025 mM to 1.0 mM. It is reasonable to expect that similar linearity would be obtained for the other amines used in this work. However, other laboratories would need to obtain their own calibration lines using their own equipment.

The detection limit was estimated to be 0.05  $\mu\text{M}$  (10 ppb) of dodecylamine with a signal/noise ratio of 3.

### 3.3. Recommended analytical procedures

Recommended analytical procedures for determining the amine concentrations in solutions from either laboratory or plant flotation operations are summarised in Fig. 4. A similar procedure can be used for the determination of amines or amine acetates in solid flotation collectors. These methods are based on the preferred conditions discussed earlier

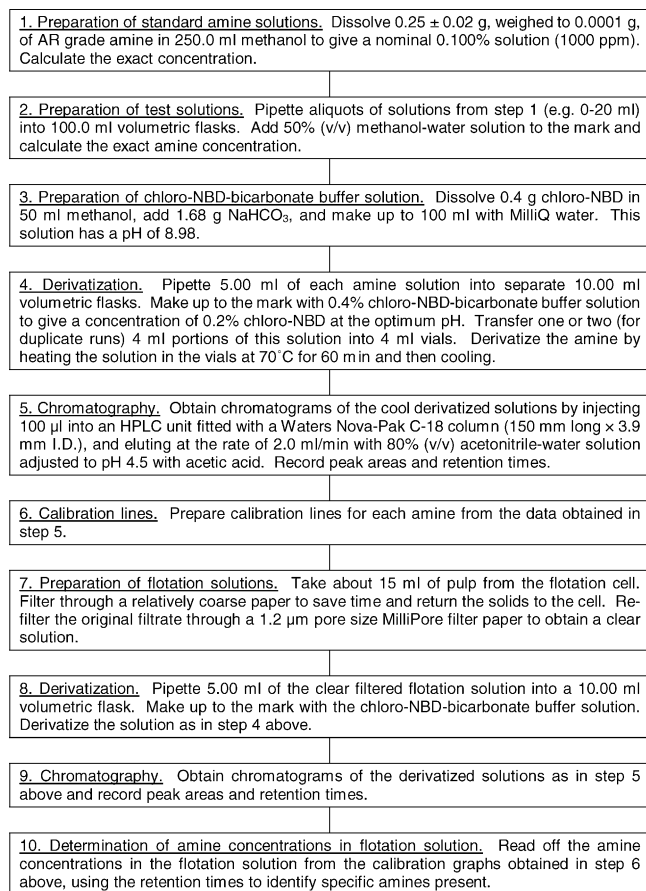


Fig. 4. Flowsheet summarizing the recommended analytical procedure for the determination of amines in flotation solutions.

in this paper. The conditions are, firstly, derivatization of the amines present with chloro-NBD at pH 8.5–8.9 for 60 min at a temperature of 70 °C to give the corresponding amino-NBDs. This is followed by chromatographic separation of unused chloro-NBD and the amino-NBDs by HPLC, and measurement of the amino-NBD concentrations by UV–vis spectroscopy at 470 nm.

### 3.4. Possible interferences with analytical methods

There are few known or likely substances that might be present in either laboratory or plant solutions that could interfere with the analytical method and no specific work has been done on them. Naturally-occurring ammonia or ammonium salts, which would be derivatized, could be present in any of the various possible water sources used in a plant. These sources include fresh water, saline bore water, mine water, and treated sewage effluent. Ammonium nitrate could be present in the ore fed to a plant if ANFO (ammonium nitrate fuel oil mixture) had been used for blasting during mining. However, the amino-NBD derivatives would be short chain varieties, which would be flushed through early in the elution cycle and be recognised as such. Any heavy metal ions present would be at very low levels.

Added flotation reagents, which could include depressants such as starch and dextrin, activators such as sodium fluoride, and frothers such as polypropylene glycol or methyl isobutyl carbinol, would not be expected to interfere, and there was no evidence from the flotation test reported later that they were interfering. Inorganic reagents such as sulphuric acid or sodium hydroxide, which are often used to adjust flotation pH, would not interfere as such, but care would need to be taken to ensure that the pH for derivatization was adjusted to the optimum level of about pH 9. Reagents such as acetic acid or hydrochloric acid, which are sometimes used to increase the aqueous solubility of an amine instead of using the acetate or chloride salt, would not be expected to have any effect, and neither would kerosene or light fuel oil, which are also sometimes used to increase the solubility of a higher amine, nor fuel oil derived from ANFO. The flotation test described in the next section specifically showed that neither sodium fluoride nor starch, which are commonly used in flotation with amine collectors, interfered with amine determinations.

## 4. Application of analytical method to flotation solutions

As shown in this section, the analytical method outlined in Fig. 4 for the determination of amines in flotation pulp solutions was successfully applied to solutions from a laboratory flotation test.

A ‘baseline’ flotation test was conducted on a mineral sand mixture of ilmenite, chromite, and quartz. This test involved standard equipment and standardized procedures that are not detailed here. Basically, the test involved first adding 200 g/t

starch (200 g/tonne based on the solids feed mass) as a depressant, 200 g/t sodium fluoride as an activator, and conditioning for 2 min after each addition. Three stages of amine flotation were then conducted by adding 200 g/t of both hexylamine and dodecylamine to each stage, conditioning for 2 min, and then floating for 2 min. This gave an estimated concentration in solution of 18.1 ppm hexylamine and of dodecylamine. Pulp samples were taken at zero time, i.e. before any reagents were added, then at 4 min, i.e. after conditioning with starch and sodium fluoride, but before the first addition of amines, then 2 min after each addition of amines, and at the end of each 2 min flotation period (eight samples in all). These pulp samples were filtered twice; once to remove the bulk of the solids and then through a Millipore membrane (1.2  $\mu\text{m}$  pore size) to remove traces of solids. These solutions were analyzed for each amine by the procedure outlined in Fig. 4. The measured values obtained are plotted as a function of time as filled circles on Fig. 5.

In addition, the theoretical concentration of each amine in solution immediately after the amine additions was calculated by adding the equivalent value of the amine addition (38.1 ppm of hexylamine and 38.1 ppm of dodecylamine) to the measured concentration just before the amine addition was made. It was assumed that the addition was made instantaneously and that perfect mixing was obtained instantly. No corrections were made for the water volume removed with the froth concentrate and replaced with fresh water through-

out the test. The calculated values obtained are plotted as a function of time as open circles on Fig. 5.

These results show, firstly, that at zero time before any reagents have been added, that the analytical method gave a zero concentration of amine, as expected. Secondly, at 4 min, after the addition of starch and fluoride but before the addition of amines, a zero amine content was also obtained. This is important in showing that these reagents do not interfere with amine determinations in the solutions involved.

After the first addition of amines, the calculated amine concentrations in solution were 38.1 ppm for both amines (0.376 mM for hexylamine and 0.206 mM for dodecylamine).

For hexylamine, the upper part of Fig. 5 shows that there was very little consumption of the amine during the test; i.e. there was little hexylamine adsorption on the mineral surfaces. With additions of amine at 4 min, 8 min, and 12 min, there is a step increase in hexylamine concentration in solution. The final measured concentration of 109 ppm hexylamine was 95% of the theoretical level of 114.3 ppm.

With dodecylamine (the lower part of Fig. 5), however, a characteristic saw-tooth shaped curve was obtained, similar to those often observed for changes in xanthate and other collector concentrations in solution in sulphide mineral flotation as reported by Jones and Woodcock [10]. This shows that roughly half of the added dodecylamine was consumed in the 2 min conditioning stage, and a further quarter in the 2 min flotation period. The amount of amine remaining after each flotation stage increases slightly with the number of stages. The concentration at the end of the third stage was 18.4 ppm dodecylamine which was about 16% of the theoretical level of 114.3 ppm, assuming no adsorption of reagent on the solid phase.

These results are generally consistent with the expected behavior of amines in an oxide flotation system containing minerals such as ilmenite and chrome spinels. Thus short chain amines (nominally  $<C_{12}$ ) are not adsorbed to any significant extent, whereas the longer chain amines (nominally  $>C_{12}$ ) are more strongly and rapidly adsorbed because the longer carbon chain imparts a greater driving force to effect adsorption.

It is believed that information of this type will be of great value in interpreting the results of amine flotation tests and guiding future work. Clearly, there is a great deal of work to be done in evaluating the effects of different variables on the kinetics and completeness of the adsorption reaction in relation to different mineral mixtures and the separation of specific minerals by differential flotation. The application of the method developed here should be of great benefit in conducting such investigations.

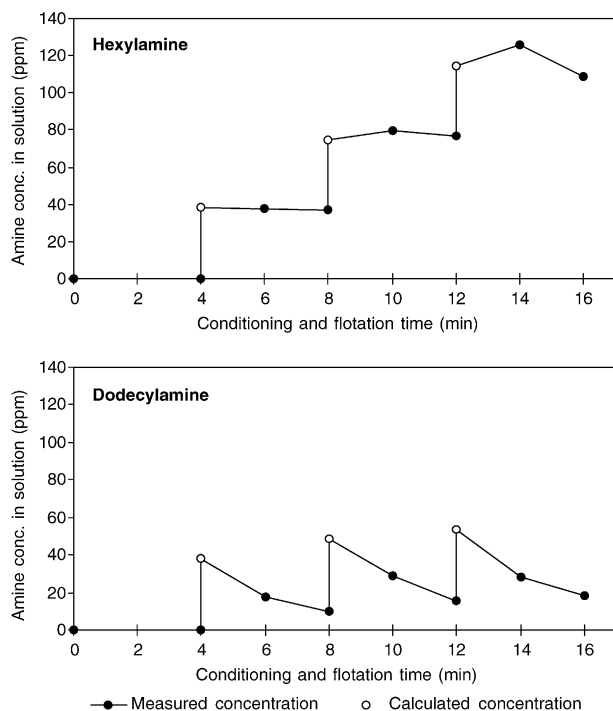


Fig. 5. Plot of hexylamine and dodecylamine concentrations in solution during a typical baseline flotation test on an ilmenite/chromite mineral sand mixture. Starch (200 g/t) added at 0 min. Sodium fluoride (200 g/t) added at 2 min. Hexylamine (200 g/t) and dodecylamine (200 g/t) added at 4, 8 min and 12 min. All reagent additions based on solid feed weight to test.

## 5. Application of the analytical method to flotation collectors

A modification of the analytical procedure for determining the concentrations of amines in flotation solutions was

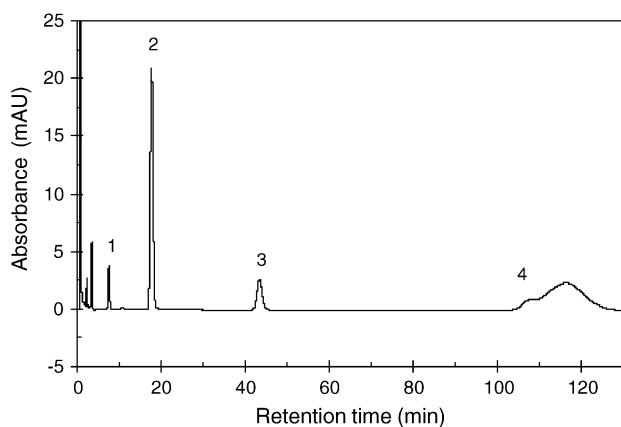


Fig. 6. Chromatogram of a derivatized commercial coco amine acetate. Numbered peaks are, respectively, (1) decylamine, (2) dodecylamine, (3) tetradecylamine, and (4) a mixture of hexadecylamine and an unidentified compound, possibly an isoamine. The first (large) un-numbered peak is the solvent peak. The second and third (small) un-numbered peaks, before the decylamine peak, are believed to be hexylamine and octylamine, respectively.

successfully applied to a sample of Armac C (a coco amine acetate) from Armour Industrial Chemical Co., Chicago, USA (now Akzo Nobel Surface Chemistry, Chicago, USA). This reagent is an oil paste amine. A suitable weight of the reagent was dissolved in methanol and then derivatized with chloro-NBD. A portion of the derivatized amino-NBD product was injected into the HPLC system and eluted with a solution containing 40 mM acetate and 80% methanol. (Note that this analysis was conducted before acetonitrile was selected as the preferred eluent.) The resultant chromatogram is shown in Fig. 6 and the estimated distribution of the amine acetates present is shown in Table 3, together with data from the reagent manufacturer (Armour) and data on a similar reagent (Flotigam CA) made by another manufacturer (Hoechst, Verkauf TH, now Clariant, Frankfurt am Main, Germany [11]).

Table 3  
Estimated proportions of amine acetates present in commercial coco amine acetates

Amine acetate	Carbon number	Proportion of amine acetates present (% , w/w)		
		Armour Armac C		Hoechst
		This work	Akzo Nobel <sup>a</sup>	Flotigam CA <sup>b</sup>
Hexyl	6	2	–	6
Octyl	8	7	5	6
Decyl	10	6	6	54
Dodecyl	12	63	50	18
Tetradecyl	14	18	19	8
Hexadecyl	16	4	10	8
Octadecyl	18	–	10	–
Total	–	100	100	100

<sup>a</sup> Data from product information sheet from Akzo Nobel Surface Chemistry, Chicago, USA.

<sup>b</sup> Data from Hoechst Verkauf TH [11].

Peaks 1, 2, and 3 on Fig. 6 from this work were positively identified as, respectively, decylamine (6.2% of the amine content), dodecylamine (63.1%), and tetradecylamine (17.5%). Peak 4 corresponds to hexadecylamine (3.5% of the amine content), but it is partly overlapped by an impurity with a slightly longer retention time, which is possibly an isoalkyl amine product.

The two small peaks after the large solvent peak at about 1 min but before peak 1 were shown by spectrometric examination of the eluent solution to be amino-NBD derivatives, but they could not be quantified at that time because there was no standard for them. However, the alkyl chain length of each of these amines was determined by a theoretical method. Injection of a mixture of aliphatic amines showed that there is a linear relation between the logarithm of the retention factor ( $\log k'$ ) and the carbon atom number ( $C$ ) of the amine.

Using this relationship to predict the retention times for amines with six ( $C_6$ ) and eight ( $C_8$ ) carbon atoms, respectively, gave 1.81 min and 3.32 min. These values are very close to the observed retention times of 2.17 min and 3.42 min, respectively for the two small peaks on Fig. 6 before peak 1. It was therefore concluded that the two unknown components in the coco amine sample used are probably hexylamine ( $C_6$ ) and octylamine ( $C_8$ ), respectively. The two amines constitute about 2% and 7% of the amines in the original reagent (Table 3).

Table 3 shows that data from the manufacturer of the Armac C are broadly similar to the data obtained in this work, but there are some differences, and data from Hoechst [11] for the Flotigam CA, which is also described as a coco amine acetate, are different again. It is believed that there are two main reasons for these differences. Firstly, it is understood that manufacturers' data sheets provide typical, not absolute, values. This is because specific batches of product vary with the actual source of the feed-stock from different coconut plantations. Secondly, the different manufacturers process and purify the original coco fatty acids with different procedures. In addition, it is known that the reagents can decompose for a variety of reasons during storage. This may have happened to the sample of Armac C used in this work. However, this indicates the value of analyzing the amine content of reagents when conducting some types of flotation research using commercial products.

## 6. Conclusions

This work has shown that a suitable method for the determination of aliphatic primary amines and amine acetates with carbon chain lengths of the amines of  $C_6$  to  $C_{18}$  is by derivatizing the amines present with 4-chloro-7-nitrobenzofurazan, separating the derivatized amines by HPLC, and measuring the concentration of each derivatized amine by UV–vis spectroscopy. The method is applicable to the determination of the concentration of the various amines in commercial or 'pure'



flotation reagents, in solutions from flotation plant pulps, and to tailing samples and other products requiring environmentally acceptable disposal. Concentrations between about 0.01 ppm and 200 ppm can be measured directly. Higher concentrations may require dilution. No interferences have been found.

Because the method can measure the concentrations of the various amines present in a flotation pulp at various times during a test, and noting that this information has not previously been readily available, it provides a valuable new tool for adjusting reagent additions to a laboratory or plant operation, and thus effecting improved reagent control, and in helping in the interpretation of the flotation results obtained.

The method could probably be adapted for on-line determination of amines in a flotation plant, and by reducing the derivatization time (with some sacrifice in accuracy) the time lag between sampling and measuring could be possibly reduced to an acceptable level for plant control. However this needs to be demonstrated. For environmental samples, the time lag would be of no consequence.

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#### References

- [1] M.H. Jones, J.T. Woodcock, in: P. Somasundaran, B.M. Moudgil (Eds.), *Reagents in Mineral Technology*, Marcel Dekker, New York, 1988, p. 683.
- [2] L.K. Wang, R.G. Ross, M.H. Wang, *Proc. Ind. Waste Conf.* 32 (1978) 165.
- [3] M. Tsubouchi, H. Mitsushio, N. Yamasaki, *Anal. Chem.* 53 (1981) 1957.
- [4] Ya.L. Kostyukovskii, F.A. Medvedev, D.B. Melamed, *J. Anal. Chem. (USSR) (English trans.)* 35 (1980) 378.
- [5] B. Sahasrabudhey, A. Jain, K.K. Verma, *Analyst* 124 (1999) 1017.
- [6] A.V. Khryashchevskii, O.A. Shpigun, P.N. Nesterenko, *J. Anal. Chem. (USSR) (English trans.)* 52 (1997) 656.
- [7] J. Verdú-Andrés, P. Campíns-Falcó, R. Herráez-Hernández, *Analyst* 126 (2001) 1683.
- [8] G. Taguchi, Y. Wu, *Introduction to Off-Line Quality Control*, Central Japan Quality Control Association, Nagaya, 1985.
- [9] D.D. Perrin, *Dissociation Constants of Inorganic Acids and Bases in Aqueous Solutions*, Butterworths, London, 1969.
- [10] M.H. Jones, J.T. Woodcock, in: M.H. Jones, J.T. Woodcock (Eds.), *Principles of Mineral Flotation—The Wark Symposium*, Australasian Institute of Mining and Metallurgy, Melbourne, 1984, p. 147.
- [11] Hoechst Aktiengesellschaft Verkauf TH, *Flotigam Grades: Cationic Collectors for the Flotation of Potash Minerals*, Hoechst, Verkauf TH, Frankfurt am Main (now Clariant, Frankfurt am Main), Germany, 1978.