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(57) Abstract: The present invention is related to a method of quantification of fatty amines derived from effluents and residues from the reverse flotation process of iron ore by a colorimetric technique with bromocresol green as the organic dye.
"AMINES QUANTIFICATION METHOD IN RESIDUES OF THE FLOTATION OF IRON ORE"

The present invention is related to a quantification method of fatty amines derived from iron ore reverse flotation process effluents and residues using the colorimetric technique and bromocresol green as an organic dye.

Due to the growing demand for iron, the iron ore deposits with high iron contents are decreasing, thus being necessary to exploit deposits with increasing lower iron contents.

Ores from high iron content deposits are only submitted to the comminution and granulometric classification. In contrast, low iron content deposits require concentration stages to obtain the required market specifications, such as minimal iron content and a reduction of undesirable substances present, such as silica.

The main concentration method used in the treatment of iron ore is reverse cationic flotation. This method separates iron oxides from silica.


After flotation, the largest part of the fatty amines used are retained in the flotate (mainly quartz) and discarded to tailing dams. The possibility of the reutilization of amines would contribute to reducing operating costs considerably, besides reducing the amount of reagents discarded to the environment. An estimated 5,500 tons of amine derivatives are used every year in Brazil [Neder, E.E. 2005. O Uso das Aminas Graxas e seus Derivados na Flotação de Minérios Brasileiros. Universidade de São Paulo. Master's Degree Dissertation, 91p]. An increase in the consumption of amines is expected in the coming years due to the world’s growing demand for iron ore. Amines are
relatively expensive reagents; however, they are important in the concentration process and may represent about 48% of the total cost of flotation reagents [Batisteli, G.M.B. 2007. Amina Residual na Flotação Catiónica Reversa de Minério de Ferro. Universidade Federal de Minas Gerais, Master’s Degree Dissertation, 118 p] and 30% of the total processing costs [Neder, 2005]. Therefore, there is great interest in the reduction of the costs of amines in iron ore processing. One of the alternatives involves the reutilization of amines used in the reverse flotation of iron ore. The invention patent DE10065846-A1 describes the only process of the reutilization of amines in the reverse flotation of iron ore published to present. The process consisted of two flotation steps. In the first step, 100% of the new amine was added. The used water from this first flotation step, which contained residual amine, was added with different proportions of amine (0 and 50%) in relation to the quantity of amine added in the first flotation step.

Although the current patent application describes this process, the inexistence of a method to quantify amine in flotate water makes it impossible to know the exact amount of amine left in the flotate water, and consequently, the amount required to be added. Therefore, besides the efforts to describe the amine recovery processes in iron ore processing, it is essential for a method of quantification of amines in flotate to evaluate if the amines are actually being recovered, and if so, the amount of amine recovered.


The colorimetric methods consist of the formation of amine salts colored by organic dye and their extraction with organic solvents. The mentioned organic dyes are soluble in aqueous solutions and insoluble in organic solvents. After reaction with the amine salts, the compound formed becomes soluble in organic solvents.

The intensity of the color formed is measured by colorimetry. A calibration curve is plotted for each of the amine compounds formed and compared to standard samples with known concentrations. These curves are used to determine the concentration of amines in samples with unknown concentrations.

Ninhydrin is a dye used in a colorimetric method that was initially used to quantify amino acids Greenstein, J.P.; Winitz, M. 1961. Chemistry of the amino acids. Ed. John Wiley & Sons, New York, vol. 2, cap. 11]. A purple
coloration is observed when the α amino acid is added to a medium containing triketohydrindene hydrate (ninhydrin), which is attributed to the formation of diketohydrindylidenediketohydrindamine. The intensity of the color is directly related to the concentration of the compounds in the solution. The purple coloration has maximum absorption in the 550-570 nm region.

Although it had been previously used in the qualitative and quantitative determination of α amino acids, ninhydrin also reacts with peptides, primary and secondary amines, ammonia, and amino alcohol, thus its use is not considered as a specific method. When used in quantitative determination, the complete removal of interferants is extremely important.


Previous studies showed that this method has good sensitivity (detection of up to 1 mL L⁻¹) and repeatability for actual-samples. However, the problem with its use is the low yield in the extraction of amines, mainly from solids [Reis, 2004] [Chaves, 2001].

The flotation of iron ore results in two products, a concentrate containing iron ore and the tailings, which are discarded to tailings dams. Part of the total amine added is lost in the solid and liquid fraction of the tailings. The effluents and tailings produced contain mainly silica, organic compounds, such as aliphatic amines (primary, secondary, and tertiary), and also significant amounts of iron ore and other metals. Normally, the flotation tailings are sent to tailings dams, which are expected to retain the solid particles.

In the state of the art, very few patents are found on amine quantification methods using colorimetric methods. Caillouette, James C., patent US5998161: "Amine detection by color change, in human body moisture," developed a method to detect amines associated to pathogenic bacteria using bromocresol green as an organic dye of amines. Beauchamp, Jesse L., patent US20060263257A1: "Optical gas sensor based on dyed high surface area substrates," developed a new optical sensor that used bromocresol green as an
organic dye. This sensor can identify aliphatic amines, such as tert-butylamine, diethylamine, and triethylamine, besides pyridine and aniline.

However, no efficient method for the quantification of amines using an organic dye different from ninhydrin for dosing fatty amines in iron ore reverse flotation effluents has been reported to present.

The current invention describes a fatty amine quantification method applicable to the iron ore flotation process using bromocresol green as a dye, aiming mainly to optimize the reutilization of amines, since it allows for identifying the accurate amount recovered in the previous process and the accurate amount to be added in the next process.

It is known that amines may form two types of compounds in the presence of bromocresol. In alkaline solutions, it forms a green diamine salt, while in acidic solutions it forms a yellow monoamine salt [Mukerjee, 1956; Auerbach, 1943]. In the present method of quantification of amines, the reaction between an etheramine and bromocresol green occurs at pH = 5; therefore, forming a monoamine salt.

The present method allows for the quantification of amines etheramine Flotigam EDA 3B and ether diamine Flotigam 2835, which are produced by Clariant and are used in the flotation process by several mining companies.

According to Clariant's datasheet [Empresa Clariant S.A. 1999. Product Data Sheet. São Paulo. 5p], the etheramines studied have the following chemical composition: [R-O-(CH₂)₃-NH₃⁺ CH₃COO⁻ (Flotigam EDA 3B) where, R = alkyl radical with com 10-14 carbon atoms and [R-O-(CH₂)₃-NH-(CH₂)₃-NH₃⁺ CH₃COO⁻ (Flotigam 2835) where, R = alkyl radical with com 10 or more carbon atoms.

This invention can be better understood with the examples below:

Example 1: Quantification of fatty amines

Starting with etheramine EDA 3B and a mixture of 25% etheramine EDA 3B and 75% of F2835 used in the reverse flotation of iron ore, calibration curves were plotted for EDA and the EDA 3B and F2835 mixture.

The colorimetric method using the bromocresol green method was thus applied. The samples were placed in a decantation funnel along with the
bromocresol green buffer at pH = 5 and chloroform. A colored chloroform-
soluble compound was formed. Absorbance can be measured with a Merck-
SQ118 spectrophotometer at 409 nm. Blanks can be prepared with distilled
water as a substitute of the amine solutions.

The method validation parameters used are the usual, such as accuracy,
precision, linearity, and limit of detection.

The method linearity is determined through the analytical curve. The
concentration of amine standards are 5, 10, 20, 30, 40, and 50 mg/L. Linearity
can be estimated through the linear regression analysis by the minimum square
method.

Precision is determined with a 3G-mg/L sample of EDA 3B prepared and
analyzed in triplicate and on five different days.

Accuracy can be evaluated by the recovery test in the triplicate of an
effluent sample from the flotation process containing starch and possible
interferants from iron ore. Three known standard concentrations of EDA 3B
were used, 10, 25, and 50 mg/L.

**Example 2: Determination of amines in effluents**

In the determination of amines in the reverse flotation of iron ore effluents
and tailings, three workbench-scale flotations were performed using the
procedures described by Stapelfeldt *et al* in XIX ENTMMME – Recife,
Pernambuco, Brazil [2002]. For that, the procedures were carried out in a
workbench flotation cell from Denver with a 2 L basin, using, for example,
1150g iron ore together with 1400 mL water. The flotation process conditions
were 1200 rpm, starch conditioning for 5 min, collector conditioning for 1 min,
and foam removal. The processes were carried out at pH = 10.5 and an amine
at a concentration of 40 g/ton (gram of amine per ton of iron ore). After the
workbench iron ore flotation, four liquid and solid fractions were obtained. All
fractions were analyzed by the proposed method with bromocresol green and
by the traditional ninhydrin method.

Amine was extracted from the solid samples before amine quantification
by mixing 10 g of tailings (obtained in the flotation tests) with 100 mL of Milli-Q
water under agitation. The suspension was filtered and the filtrate was analyzed
to determine the amount of desorbed amine, according to the procedures described for bromocresol and ninhydrin.

Table 1 shows the analytical curve data for EDA 3B and the EDA 3B and F 2835 mixture. The analytical curve was linear in the range 5.0-50 mg/L in both cases.

Table 1. Linear regression analysis of the analytical curve of EDA 3B and the EDA 3B and F 2835 mixture.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>EDA 3B</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration range (mg/L)</td>
<td>5.0-50.0</td>
<td>6.5-65.0</td>
</tr>
<tr>
<td>Curve equation (n = 3)</td>
<td>$y = 0.0217x + 0.0543$</td>
<td>$y = 0.0219x - 0.0141$</td>
</tr>
<tr>
<td>Determination coefficient</td>
<td>0.9993</td>
<td>0.9979</td>
</tr>
</tbody>
</table>

The precision evaluation results are given in Table 2. The variation coefficient obtained for bromocresol green shows that the method precision is satisfactory. The variation coefficient of the traditional ninhydrin method was rather high, showing that it is not as efficient as the method with bromocresol green in the quantification of amines in iron ore reverse flotation effluents.

Table 2. Evaluation of precision of the bromocresol green (BROMOCRESOL GREEN) and ninhydrin (NINHYDRIN) methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Concentration (mg/L)</th>
<th>n</th>
<th>Variation coefficient (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NINHYDRIN</td>
<td>58</td>
<td>5</td>
<td>37.70</td>
</tr>
<tr>
<td>BROMOCRESOL GREEN</td>
<td>36</td>
<td>5</td>
<td>3.53</td>
</tr>
</tbody>
</table>

Table 3 gives the method accuracy results obtained for bromocresol green. The recovery values of the proposed method were considered as acceptable. The method has good selectivity for the quantification of fatty amines in the matrix used. To confirm the precision of the method, the Student test at 95% confidence and n-1 degrees of freedom was used. The calculated t values (Table 3) for the concentrations studied gave values smaller than the theoretical t value (2.776); therefore, there was not a significant difference between the calculated and theoretical values; emphasizing that the
concentrations studied are within the concentration range of amines in iron ore effluents.

Table 3. Recovery of the standard solutions of the EDA 3B added to the samples and analyzed by the bromocresol green method. (n = 5)

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Recovery (%)</th>
<th>Variation coefficient (%)</th>
<th>$t_{calculated}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>97.30</td>
<td>2.74</td>
<td>-2.03</td>
</tr>
<tr>
<td>25</td>
<td>98.97</td>
<td>3.30</td>
<td>0.6</td>
</tr>
<tr>
<td>50</td>
<td>99.31</td>
<td>2.28</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Example 3: Flotation Test

The flotation tests were carried out with the products quantified by the bromocresol green and the ninhydrin methods. The flotation tests gave four products, two were solid and two were liquid. The results are given in Table 4. The amount of amine used in the flotation tests was 40 g/ton, which corresponds to the addition of 46 mg amine. The total recovery for the bromocresol green method was 45.33 mg on average, which corresponds to an efficiency of 98.5%. In contrast, for the ninhydrin method, the recovery was 22.01 mg of the total added, an efficiency of approximately 48%.

The results presented in Table 4 show that the bromocresol green method is more efficient in the quantification of amines in iron ore flotation tailings. The results of quantification of the solid samples by the two methods are quite different, and apparently, it is not only due to the ninhydrin method, but mainly to the method of extraction of amine from the solid residue.

Although it is extensively described in literature, the ninhydrin method proved to be inadequate in the quantification of amines, mainly in flotate solid samples. The bromocresol green method was more accurate and precise than the ninhydrin method.
Table 4. Yield of extraction for the bromocresol and ninhydrin methods.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extracted amide BROMOCRESOL GREEN (mg)</th>
<th>Extracted amine NINHYDRIN (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid flotate</td>
<td>14.52</td>
<td>13.16</td>
</tr>
<tr>
<td>Liquid concentrate</td>
<td>3.91</td>
<td>5.03</td>
</tr>
<tr>
<td>Solid flotate</td>
<td>21.04</td>
<td>9.00</td>
</tr>
<tr>
<td>Solid concentrate</td>
<td>5.86</td>
<td>0.93</td>
</tr>
<tr>
<td>Total extracted</td>
<td>45.33</td>
<td>22.01</td>
</tr>
</tbody>
</table>

Thus, the proposed quantification method of fatty amines derived from iron ore reverse flotation process effluents using the colorimetric technique and bromocresol green as an organic dye is efficient.
CLAIMS

1. Method for the quantification of amines in iron ore flotation effluents and residues by the colorimetric technique characterized by the use of bromocresol green as an organic dye.

2. Method for the quantification of amines in iron ore flotation effluents and residues by the colorimetric technique, according to claim 1, characterized by the quantification of fatty amines and eteramines.

3. Method for the quantification of amines in iron ore effluents and residues by the colorimetric technique, according to claim 1 or 2, is characterized by the reaction between the amine and bromocresol green at pH in the range from 3 to 6, mainly at pH = 5, forming a monoamine salt.

4. Use of the colorimetric technique to quantify amines is characterized by the quantification of fatty amines derived from iron ore effluents and residues submitted to reverse flotation process using bromocresol green as an organic dye.