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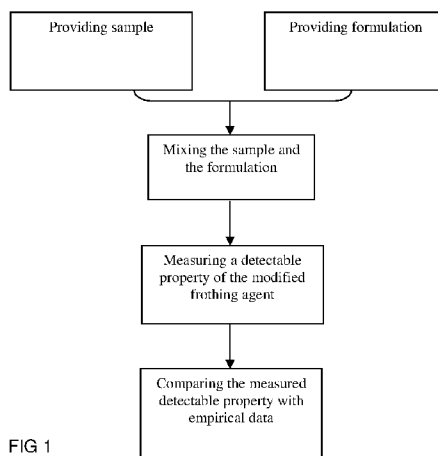


FIG 1

(57) Abstract: The present invention relates to a method and apparatus for determining the concentration of a frothing agent in a sample. The present invention alleviates the problems associated with excess frothing agent and insufficient frothing agent in the sample.

TITLE

Determination of the Concentration of Frothing Agent

FIELD OF THE INVENTION

5 [0001] The present invention relates to the field of manufacturing and mining. More particularly, the invention relates to a method and an apparatus for determining the concentration of a component in a sample. Most particularly, the invention relates to a method and apparatus for determining the concentration of a frothing agent.

10

BACKGROUND TO THE INVENTION

[0002] Any reference to background art herein is not to be construed as an admission that such art constitutes common general knowledge in Australia or elsewhere.

15 [0003] A frothing agent is an agent that is able to change the surface properties of a liquid and can result in froth after agitation. Froth comprises a mass of bubbles, and the presence and manipulation of it can be an important factor in many industries. Minerals make up a small percentage of the earth and are typically found in ore which comprise minerals, dirt and soil. Froth flotation
20 utilizes collectors that bind to, and increase the hydrophobicity of, the valuable minerals so that the minerals rise to the surface with the froth. Froth flotation also utilizes frothing agents which stabilize the froth.

[0004] A typical process of froth flotation includes the reduction of the size of the ore through crushing and grinding. The crushed ore is then added to water to
25 which collectors and frothing agents are added. The mixture is then agitated to form froth. The froth, and the collector-bound minerals, rise to the surface due to their hydrophobicity and this effectively separates the desirable minerals from the dirt, soil and other minerals. The froth is then collected and treated to isolate the desirable mineral, and the process water is reused.

[0005] Froth also occurs in other industrial processes, sometimes as an undesirable by-product. For instance, froth occurs in food processing and can have an undesirable effect in the manufacture of food due to processability issues. In this respect, it is desirable to minimize the amount of froth. The presence of froth can also have a significant effect on experimental reactions in the life sciences. In response, anti-frothing agents are added to minimize the amount of froth. However, the addition of insufficient anti-frothing agent will not remove froth from the reaction, while the addition of excess anti-frothing agent may itself have an adverse effect on the reaction. It is therefore desirable to develop a method to accurately determine the concentration of a frothing agent.

[0006] In mining, frothing agents at appropriate concentration levels can produce desirable bubble size, stability and mobility of the froth phase, which in turn affects the kinetic viability of the flotation process and the separation efficiency. A problem encountered is that a residual amount of frothing agent remains in the process water even after froth has been removed. As the process water is reused, the residual frothing agent can have an impact further downstream, such as causing over-frothing in pumps and sumps. It is also wasteful to utilize more frothing agent than required.

[0007] On the other hand, insufficient frothing agent addition results in a loss of yield and efficiency. Typically, excess frothing agent is added to ensure that essentially all of the collector-bound minerals are brought to the surface. As such there is, at least, residual frothing agent in the remaining process water. Therefore, a quick and effective method of determining the concentration of frothing agent is desirable to alleviate these problems.

[0008] Calculation of the concentration of the frothing agent is difficult due to factors such as incomplete dissolution and the unknown distribution of the frothing agent. The existing techniques for determining the concentration of frothing agent are ineffective and inaccurate. Typical techniques for determining the concentration of a frothing agent require a sample to be removed from a processing line, the sample is then transported to a laboratory to be tested, and then the results are sent back. This process can take several hours to overnight

and it should be clear that this delay is undesirable as real time optimization is not possible.

[0009] Hart *et al.* (Hart, G., Attalla, M., and Morgan, P. (2006) *ACARP project C 13056*) designed an atmospheric alcohol detector which measures the amount of alcohol in the atmosphere. Frothing agents generally have an alcohol functionality and evaporate into the atmosphere. The atmospheric alcohol detector measures the amount of alcohol in the atmosphere and correlates this measurement to a concentration of frothing agent. The atmospheric alcohol detector is limited to short chain alcohols with high evaporation rates (e.g., 4-methyl-2-pentanol, 'MIBC'). Furthermore, the atmospheric alcohol detector has a high degree of variation and the results can depend on the ambient conditions, such as temperature, pressure and humidity.

[0010] Lahey and Clarkson developed a method of determining the concentration of a frothing agent (Lahey, A., Clarkson, C. (1999) *ACARP Report C 6045*) by measuring froth height. Froth height measurement involves agitating a sample to measure the height of the froth. The height of the froth is then used to determine the concentration of frothing agent. This method has poor reproducibility, is dependent on the ambient conditions, and can be affected by the presence of salts, flocculants, collectors and oils. Further to this, this method is not suitable for residual amounts of frothing agent.

[0011] Gelinas *et al.* (Gelinas, S., and Finch, J. A. (2005) *Minerals Engineering*, 18(2), 263-266) developed a colorimetric technique which utilized a reaction between the alcohol functionality of a frothing agent with concentrated sulphuric acid, and salicylaldehyde. The reaction resulted in a coloured solution which could be analysed using UV-visible spectrophotometry. However, this technique had a low analysis rate and required hours to obtain a result. Further to this, the use of hazardous chemicals such as concentrated sulphuric acid is undesirable due to safety concerns.

[0012] It should be apparent that there is a need for an apparatus and method to determine the concentration of a frothing agent in a sample that alleviates the disadvantages discussed above.

SUMMARY OF THE INVENTION

5 [0013] In a first form, although it need not be the only or indeed the broadest form, the invention resides in an automated method for determining the concentration of a frothing agent in a sample comprising the steps:

- a. drawing a sample with an unknown concentration of frothing agent from a line in a production plant;
- 10 b. adding a formulation to the sample;
- c. mixing the sample and the formulation to form a modified frothing agent having a detectable property;
- d. measuring and quantifying the detectable property; and
- e. comparing a measured detectable property of the modified frothing
15 agent with a database of known empirical data to determine the concentration of the frothing agent in the sample.

[0014] The frothing agent is suitably an alcohol or a glycol. The frothing agent may suitably be 4-methylpentan-2-ol (MIBC), 4-methylcyclohexanemethanol (MCHM) or 1-(2-methoxy-1-methylethoxy)propan-2-
20 ol (DowFroth250).

[0015] The formulation comprises one or more components selected from the group consisting of polyaromatic hydrocarbons, compounds with a cavity to accommodate a frothing agent, and indicators.

[0016] The polyaromatic hydrocarbon is suitably pyrene.

25 [0017] The compound with a cavity to accommodate a frothing agent is suitably β -cyclodextrin.

[0018] The indicator is selected from the group consisting of phenolphthalein, crystal violet, and congo red.

5 [0019] The formulation further comprises one or more solvents. The solvent may be a polar solvent or a non-polar solvent. The solvent is selected from the group consisting of water and alkyl alcohols. In one form, the water is deionized water. Preferably, the solvent is deionized water or alkyl alcohol or a combination thereof.

[0020] In one aspect, the formulation comprises pyrene, β -cyclodextrin and water.

10 [0021] In another aspect, the formulation comprises pyrene, β -cyclodextrin, water and methanol.

[0022] In a certain aspect, the formulation comprises pyrene, β -cyclodextrin and methanol.

15 [0023] In yet another aspect, the formulation comprises phenolphthalein, β -cyclodextrin and deionized water.

[0024] In an aspect, the detectable property is selected from the group consisting of electrochemical properties and optical properties.

[0025] In a second form, the invention resides in an apparatus for determining the concentration of a frothing agent in a sample comprising:

20 a mixing chamber having a sample inlet and at least one formulation inlet; and

an analyser connected to the mixing chamber, the analyser having at least one detector that measures at least one detectable property;

25 wherein a sample is drawn from a line in a production plant and introduced to the mixing chamber through the sample inlet and a formulation is introduced to the mixing chamber through the at least one formulation inlet, and

wherein the formulation and the frothing agent form a modified frothing agent that exhibits the detectable property.

[0026] The frothing agent is suitably an alcohol or a glycol.

[0027] The formulation is as substantially described in the first form.

5 [0028] In one aspect, the detectable property is selected from the group consisting of electrochemical properties and optical properties.

[0029] In another aspect, the at least one detector is selected from the group consisting of electrochemical detectors and optical detectors.

10 [0030] The various features and embodiments of the present invention referred to in the individual sections above and in the description which follows apply, as appropriate, to other sections, *mutatis mutandis*. Consequently features specified in one section may be combined with features specified in other sections as appropriate.

15 [0031] Further features and advantages of the present invention will become apparent from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

20 [0032] To assist in understanding the invention and to enable a person skilled in the art to put the invention into practical effect, preferred embodiments of the invention will be described by way of example only with reference to the accompanying drawings, in which:

FIG 1 is a flow chart of the steps of a method for determining the concentration of a frothing agent in a sample;

25 FIG 2 shows the absorbance of MIBC and a formulation (pyrene, β -cyclodextrin and deionized water) at different wavelengths;

FIG 3 shows a graphical representation of the absorbance of a formulation (pyrene, β -cyclodextrin and deionized water) mixed with MIBC or MCHM vs concentration;

FIG 4 shows the effect of agitation time on absorbance;

FIG 5a shows absorbance (ABS) vs MIBC at different concentrations with a formulation (pyrene, β -cyclodextrin and deionized water);

5 FIG 5b shows change in absorbance (Δ ABS) vs MIBC at different concentrations with a formulation (pyrene, β -cyclodextrin and deionized water);

FIG 6 shows the effect of flocculent concentration on absorbance;

FIG 7 shows the effect of electrolyte concentration on absorbance;

10 FIG 8 shows the effect of the addition of α -cyclodextrin on the absorbance of diesel;

FIG 9 shows the effect of collector concentration on absorbance;

FIG 10 shows Δ ABS vs MIBC at different concentrations with a formulation (pyrene, β -cyclodextrin, deionized water and methanol);

15 FIG 11 shows Δ ABS vs MIBC at different concentrations (0 ppm to 1 ppm) with a formulation (pyrene, β -cyclodextrin, and pure methanol);

FIG 12 shows Δ ABS vs MIBC at different concentrations (0 ppm to 3 ppm) with a formulation (pyrene, β -cyclodextrin, and pure methanol);

FIG 13 shows a schematic diagram of an apparatus for determining the concentration of frothing agent in a sample;

20 FIG 14 shows a schematic diagram of another embodiment of an apparatus for determining the concentration of multiple frothing agents in a sample;

FIG 15 shows the Δ ABS of added salts and flocculants to a real process water sample; and

25 FIG 16 shows the effect of α -cyclodextrin used to suppress diesel in a real process water sample.

DETAILED DESCRIPTION OF THE INVENTION

[0033] Embodiments of the present invention reside primarily in a method and apparatuses for determining the concentration of a frothing agent in a sample. Accordingly, the method steps and apparatuses have been illustrated in
5 concise schematic form in the drawings, showing only those specific details that are necessary for understanding the embodiments of the present invention, but so as to not obscure the disclosure with excessive detail that will be readily apparent to those of ordinary skill in the art having the benefit of the present description.

10 [0034] The term 'frothing agent' as used herein refers to a surfactant that can change the surface properties of a liquid to form, and stabilize, bubbles.

[0035] The term 'modified frothing agent' as used herein refers to a frothing agent that has complexed to, or has reacted with (e.g., through a substitution or addition reaction), a formulation.

15 [0036] The term 'detectable property' as used herein refers to a property that was not previously detectable in the unmodified frothing agent and/or formulation, and is now detectable in the modified frothing agent. Alternatively, the term 'detectable property' can also refer to a property that has a significantly higher reading in the modified frothing agent compared to the unmodified
20 frothing agent and/or formulation. The detectable property is measured using methods known to those skilled in the art. The detectable property is suitably an electrochemical property or an optical property. The detectable property can be a change in conductivity of the sample, a colour change in the sample, a change in fluorescence properties in the same, a change in the absorbance properties in
25 the sample, a change in fluorescence intensity, or a change in fluorescence lifetime and absorbance. The person skilled in the art will appreciate that the list provided merely lists the types of properties that can be the detectable property and that this list is not an exhaustive list.

30 [0037] The term 'processing plant' as used herein refers to a facility where raw materials are treated or prepared. The term 'processing plant' may be interchangeable with the term 'production plant' and vice versa. For instance, a

non-exhaustive list of processing plants include froth flotation processing plants, food processing plants, manufacturing processing plants, and chemical plants. In particular, processing plants include mineral processing plants, coal processing plants, paper recycling plants and waste-water treatment plants.

5 [0038] In this specification, adjectives such as first and second, and the like may be used solely to distinguish one element or action from another element or action without necessarily requiring or implying any actual such relationship or order. Words such as “comprises” or “includes” are intended to define a non-exclusive inclusion, such that a method or apparatus that comprises a list of
10 elements does not include only those elements but may include other elements not expressly listed, including elements that are inherent to such a method or apparatus.

[0039] It will be appreciated that the method and apparatus are discussed in relation to froth flotation for simplicity, however, the method and apparatus can
15 also be used in determining the concentration of a frothing agent in other process such as those in the food industry, the pharmaceutical industry and the manufacturing industry.

[0040] The invention resides in an automated method for determining the concentration of a frothing agent in a sample. Referring to FIG 1 there is shown
20 a flow chart outlining the steps of a method for determining the concentration of a frothing agent in a sample. The first step of the process is to draw a sample, with an unknown concentration of frothing agent, from a line in a production plant. The sample may comprise a frothing agent, and can be drawn from any stage of a froth flotation process. Frothing agents have a functional group that
25 affects the surface properties of a liquid. The frothing agent can have a functional group selected from the group consisting of an alcohol and a glycol.

[0041] The second step of the process is adding a formulation. The formulation comprises one or more chemical compounds. The formulation is selected based on the frothing agent in the sample.

30 [0042] The stoichiometric ratio of the formulation to the frothing agent in the sample should be greater than 1:1, suitably from about 50:1 to about 1.1:1,

preferably from about 20:1 to about 1.1:1, more preferably from about 5:1 to about 1.1:1, and most preferably about 1.1:1.

[0043] An excess of formulation to frothing agent results in substantially all of the frothing agent being converted to modified frothing agent, and so the measurement and quantification of a detectable property of the modified frothing agent is directly dependent on the concentration of the frothing agent, as is discussed in more detail hereinafter.

[0044] The process may further comprise the step of filtering the sample. In this regard, some samples may require filtration to remove insoluble particulate matter from the sample. The filter has a pore size of suitably between about 0.1 μm and about 2 μm , more suitably between about 0.2 μm and about 1 μm , preferably between about 0.3 μm and about 0.7 μm , more preferably between about 0.4 μm and about 0.5 μm , and most preferably about 0.45 μm .

[0045] The third step of the process is mixing the formulation and the sample, with frothing agent therein, to form a modified frothing agent. The modified frothing agent has a measurable and quantifiable detectable property.

[0046] In a fourth step of the process, the detectable property is measured and quantified by a detector in the analyzer.

[0047] In a fifth step of the process, the measured detectable property of the modified frothing agent is compared to a database of known empirical data to determine the concentration of frothing agent in the sample, as is discussed hereinafter.

[0048] It is postulated that different frothing agents require different formulations to form modified frothing agents that exhibit a detectable property. For example, it will be appreciated that the reactive chemistry of an alcohol is different to the reactive chemistry of a glycol, and therefore different formulations may be required for different frothing agents.

[0049] The formulation comprises components selected from the group consisting of polyaromatic hydrocarbons, compounds with a cavity to accommodate a frothing agent, indicators and solvents.

[0050] Non-limiting examples of the polyaromatic hydrocarbon include pyrene, acridine and derivatives thereof. In one embodiment, the polyaromatic hydrocarbon is pyrene. The compound with a cavity to accommodate a frothing agent is suitably β -cyclodextrin. The indicator may include naphthalenesulfonates, azo dyes and triphenylmethane derivatives. Non-limiting examples of the naphthalenesulfonates include amaranth dye, surmain and congo red. Non-limiting examples of the azo dye include aniline yellow and 4-hydroxyphenylazobenzene. Non-limiting examples of the triphenylmethane derivatives include *o*-cresolphthalein, thymolphthalein, phenol red, fluorescein, aurin, crystal violet and phenolphthalein. In one embodiment, the indicator is selected from the group consisting of amaranth dye, surmain, aniline yellow, 4-hydroxyphenylazobenzene, *o*-cresolphthalein, thymolphthalein, phenol red, fluorescein, aurin, crystal violet and phenolphthalein, crystal violet, and congo red. The solvent is selected from the group consisting of water and alkyl alcohols. The person skilled in the art will understand that the lists provided are not exhaustive lists, but merely demonstrate the types of compounds that can be used. As used herein, the term 'alkyl alcohol' refers to a straight-chain or branched alkyl group containing at least one alcohol functionality. The alkyl may contain 1 to about 5 carbon atoms, preferably 1 to about 3 carbon atoms, more preferably 1 to about 2 carbon atoms, and most preferably from 1 carbon atom. Examples of alkyl alcohol include methanol, ethanol, propanol, isopropanol, *n*-butanol, *sec*-butanol, isobutanol, *tert*-butanol, pentanol and the like.

[0051] Non-limiting examples of the frothing agent include MIBC (4-methylpentan-2-ol), MCHM (4-methylcyclohexanemethanol) and DowFroth250 (1-(2-methoxy-1-methylethoxy)propan-2-ol).

[0052] In one example, when the frothing agent is MIBC then the formulation comprises a polyaromatic hydrocarbon, a compound with a cavity to accommodate the frothing agent and a solvent. Specifically, in this example, the polyaromatic hydrocarbon is pyrene, the compound with a cavity to accommodate MIBC is β -cyclodextrin and the solvent is water and/or alkyl alcohol.

[0053] This formulation and MIBC resulted in the formation of a ternary

complex which is measurable and quantifiable using UV-Vis spectroscopy. It was found that the detectable property (UV-Vis absorbance) increased with MIBC concentration. FIG 2 shows the detectable property (UV-Vis absorbance at 340 nm), of MIBC complexed with the formulation, increasing with concentration. It will be appreciated that other modified frothing agents can exhibit different optical properties at different wavelengths.

[0054] The % by weight amount of pyrene in the formulation comprising pyrene, β -cyclodextrin and deionized water is suitably between about $1 \times 10^{-7}\%$ and about $1 \times 10^{-5}\%$, preferably between about $3 \times 10^{-6}\%$ and about $9 \times 10^{-6}\%$, more preferably between about $5 \times 10^{-6}\%$ and about $8 \times 10^{-6}\%$, and most preferably about $7 \times 10^{-6}\%$. The % by weight amount of β -cyclodextrin in this formulation is suitably between about 0.1% and about 2%, preferably between about 0.5% and about 1.5%, more preferably between about 0.5% and about 1%, and most preferably about 0.9%. The % by weight of deionized water in this formulation is suitably between about 99% to about 99.9%, preferably between about 99.1% to about 99.5%, and most preferably about 99.5%.

[0055] In one embodiment, the compound with a cavity to accommodate a frothing agent is able to form hydrogen bonds with the frothing agent. For example β -cyclodextrin is able to form hydrogen bonds with MIBC.

[0056] It is postulated that when the frothing agent is DowFroth 250 then the formulation may comprise an indicator, a compound with a cavity to accommodate a frothing agent, and a solvent. Specifically, it is postulated that the formulation may comprise phenolphthalein, β -cyclodextrin and water. DowFroth 250 is a glycol ether, more specifically a polypropylene glycol ether.

[0057] In another example, when the frothing agent is MCHM then the formulation comprises pyrene, β -cyclodextrin and deionized water. In this regard, the modified frothing agent was found to have a detectable property (UV-Vis absorbance) which was measurable and quantifiable. The measured detectable property was found to increase with MCHM concentration. The increments of the detectable property to increasing MCHM concentration were found to be smaller than the increments of the detectable property in the corresponding MIBC trial

(FIG 3) possibly due to the bulky carbon chain.

[0058] Presented in Table 1 are the formulations that have been found, or are postulated, to be compatible with certain frothing agents.

Frothing agent	Formulation
MIBC and MCHM	Pyrene, β -cyclodextrin and deionized water;
DowFroth250 (PPG)	Phenolphthalein, β -cyclodextrin and deionized water

Table 1 – Compatible formulations and frothing agents

5 [0059] Ideally the detectable property should be undetectable in the formulation, because it may be difficult to determine the difference between the amount of detectable property that arises from the formulation and the amount of the same detectable property that arises from the modified frothing agent. Alternatively, the detectable property in the modified frothing agent should be
10 significantly greater than the detectability of the formulation to minimize the interference from the formulation.

[0060] The reaction time, or the complexing time, of the formulation and the frothing agent is within minutes of mixing and results in a high analysis rate. The rate of reaction, or complexation time, between the formulation and the frothing
15 agent is high and so the modified frothing agent can be measured shortly after mixing. This high rate of reaction alleviates the problems associated with the delay in obtaining results. The high analysis rate allows the measured detectable property to be compared to empirical data in real time and allows the method to be used in online froth analysis, as is discussed hereinafter.

20 [0061] The inventors have found that the sample and the frothing agent therein form a modified frothing agent with the formulation within a minute. To this end the inventors measured the detectable property after 1 minute, 15 minutes, 1 hour and 17 hours of agitation. These results (FIG. 4) showed that there was no significant difference in the absorbance measurement with longer

agitation time, and indicates that the modified frothing agent was formed within a minute.

[0062] A database of empirical data was prepared based on different formulations and different frothing agents. The database of empirical data comprises gradients of calibration slopes of different detectable properties for different combinations of frothing agents and formulations. For instance, the database may comprises the gradients of the calibration slopes of MIBC and MCHM with a formulation comprising pyrene, β -cyclodextrin and deionized water, as shown in FIG 3. The concentration of the frothing agent is determined by comparing the quantified and measured detectable property to the associated calibration slope in the database. The determination of the concentration of the frothing agent is completed in real time so there is little to no delay.

[0063] For example, the calibration curves of MIBC were prepared by testing different concentration of MIBC with a formulation comprising pyrene, β -cyclodextrin and deionized water. In this regard, FIG 5a shows the absorbance at 340 nm as a function of MIBC concentration with a formulation. It should be apparent that the absorbance (ABS) increased with MIBC concentration in a generally linear relationship. The inventors noted that by converting the absorbance (ABS) to change in absorbance values (Δ ABS), the calibration curve resulted in more reproducible results and less deviation between trials (FIG. 5b). In this regard, the Δ ABS values took into consideration the absorbance of a blank reference solution using the following formula:

$$\Delta\text{ABS} = \text{ABS}_{340\text{nm, solution}} - \text{ABS}_{340\text{nm, blank}}$$

[0064] It has been found that the formation of the modified frothing agent, and the sensitivity of the detectable property, is not significantly affected by the presence of flocculants (FIG 6), or electrolytes (FIG 7). This alleviates the problems associated with the impurities present in the froth flotation process.

[0065] As previously mentioned collectors are added to bind to, and increase the hydrophobicity of, the minerals. The collectors allow the minerals to float to the surface with the frothing agent. A typical collector used in froth flotation (more specifically coal flotation) is diesel. The concentration of residual diesel in

process water is typically very low (e.g. less than 1 ppm). It is known in the art that the presence of diesel contributes to an increase in the absorbance of the sample. To suppress the interference of diesel, additional reagents can be added. In this regard, α -cyclodextrin was added. The diesel complexed with α -cyclodextrin as opposed to β -cyclodextrin. The α -cyclodextrin has a cavity which accommodates the alkane molecule, and therefore inhibits its complexation with β -cyclodextrin. FIG 8 shows the effects of α -cyclodextrin addition on absorbance under various conditions. It was found that the absorbance of diesel was suppressed to almost 0 when α -cyclodextrin was added to the sample prior to the addition of the formulation. In this regard, the method may further comprise the step of pre-treating the sample. This pre-treatment may include filtration and/or adding suppressants that suppress the detectable properties of impurities.

[0066] Another common class of collectors is the alkyl xanthates. The concentration of alkyl xanthates in the process water is typically in the range of 0.1 – 2 ppm (approximately 1×10^{-6} - 1×10^{-5} M). It was found that within this concentration range the absorbance values were close to 0, suggesting that the use of the present analytical methods to measure the concentration of residual frothing agent is not subjected to interference from alkyl xanthates (FIG 9).

[0067] It will be appreciated that the formulation may further comprise a suppressant that suppresses the effect of an impurity exhibiting the detectable property. Therefore, the interference of an impurity in the sample can be minimized. For instance, α -cyclodextrin is a suppressant that suppresses the absorption of diesel. Other suppressants will be known to the person skilled in the art, and these can be added to the formulation. Alternatively, the suppressants can be used to pre-treat the sample prior to mixing with the formulation

[0068] As the formulation only reacts or complexes with a specific functional group, this method can be used to determine the concentration of a single frothing agent in a sample with a blend of frothing agents. In this respect, multiple formulations are added and mixed with the sample so that different

frothing agents form different modified frothing agents. Each of these modified frothing agents have a different detectable property which are individually measured, quantified and compared to empirical data to determine the concentration of each frothing agent.

5 [0069] It should be noted that the frothing agent concentrations of the calibration curves discussed hereinabove are the concentration of the final aqueous solution (e.g., the concentration of the frothing agent in the total volume of the sample and the formulation). The concentration and calibration curves discussed hereafter relate to the concentration of frothing agent in the sample
10 only and do not include the volume of formulation mixed with the sample.

[0070] It appears that by adding an alkyl alcohol, such as methanol, the accuracy of this process can be further improved. In this regard, FIG. 10 shows the Δ ABS at different MIBC concentrations (ranging from about 0 to 10 ppm) with a formulation. The formulation used in this example comprised of pyrene, β -cyclodextrin, water and methanol. Through the addition of methanol, the
15 accuracy of the process was improved to 0.9 ppm.

[0071] Additionally, the measuring accuracy of the process could be further improved to 0.6 ppm or better by using pure methanol as the solvent. In this regard, the formulation comprised of pyrene, β -cyclodextrin and methanol. FIG
20 11 and 12 shows the Δ ABS at different MIBC concentrations (ranging from 0 ppm to 1 ppm, and 0 ppm to 3 ppm) with the formulation. The frothing agent concentration in processing plants is expected to be low (e.g., less than 1 to 2 ppm), and so the present process is sufficiently sensitive to measure residual frothing agent concentration in processing plants.

25 [0072] In one embodiment, the measuring accuracy of the method is suitably less than 2 ppm, more suitably less than 1.5 ppm, preferably less than 0.9 ppm, more preferably less than 0.6 ppm, even more preferably less than less than 0.4 ppm, and most preferably less than 0.2 ppm.

[0073] The invention also resides in an apparatus for determining the
30 concentration of a frothing agent in a sample. Referring to FIG 13 there is shown a schematic diagram of an apparatus for determining the concentration of a

frothing agent in a sample. Apparatus 100 comprises a mixing chamber 110 and an analyzer 120. The mixing chamber 110 comprises a sample inlet 111 and a formulation inlet 112, and the analyzer 120 comprises a detector 121.

[0074] The formulation and the sample are as substantially described hereinabove.

[0075] A sample of process water, with an unknown concentration of frothing agent, is drawn from a line in a production plant and introduced to the mixing chamber 110 through the sample inlet 111, and a formulation is introduced to the mixing chamber 110 through formulation inlet 112. The mixing chamber 110 facilitates the complexation or the reaction between the sample, and thus the frothing agent therein, with the formulation to form a modified frothing agent. The mixing chamber 110 has a means for facilitating mixing. In one form, the mixing chamber comprises a stirrer, or a coil, or a high shear inline mixer. The person skilled in the art will understand that the list provided merely demonstrates the means in which mixing is facilitated and that the list is not an exhaustive list of the types of mixing means. The mixing chamber may further include a heater which can assist in the formation of the modified frothing agent.

[0076] The formulation and the sample are mixed in the mixing chamber 110 for a short amount of time to form the modified frothing agent. The mixing time is suitably less than 5 minutes, more suitably less than 3 minutes, preferably less than 2 minutes, more preferably less than 1 minute, and most preferably less than 30 seconds.

[0077] The mixing chamber 110 is connected to an analyzer 120 that comprises a detector 121. The detector 121 measures a detectable property of the modified frothing agent. This measured detectable property is then compared to a database containing known empirical data to determine the concentration of a frothing agent.

[0078] The detector 121 is a device that measures the detectable property. For instance, the detector 121 is selected from the group consisting of electrochemical detectors, or optical detectors.

[0079] An electrochemical detector measures a change in conductivity of the

sample and this is then used to determine the concentration of the frothing agent. For instance, the modified frothing agent may be a salt and therefore affect the conductivity of the sample. The electrochemical detector is compatible with modified frothing agents which have electrochemical properties. In one
5 embodiment, the electrochemical detector is selected from the group consisting of voltmeters, ammeters, potentiostats and galvanostats.

[0080] An optical detector measures a change in optical properties. The optical detector is compatible with modified frothing agents which exhibit a change in optical properties compared to the unmodified frothing agents and
10 formulation. For example, the optical detector is compatible with modified frothing agents which have a distinct colour, or have distinct absorbance or fluorescence characteristics at certain wavelengths. In one embodiment, the optical detector is selected from the group consisting of UV-Visible detectors, fluorescence spectrometers and other spectrophotometers.

[0081] The person skilled in the art will understand that the lists provided are not exhaustive lists but lists that merely exemplify the types of detectors that can be utilized.

[0082] Referring to FIG 14 there is shown a schematic diagram of another form of an apparatus for determining the concentration of a frothing agent in a
20 sample. The apparatus 200 comprises a mixing chamber 210, and an analyzer 220. The mixing chamber 210 comprises a sample inlet 211, a first formulation inlet 212 and a second formulation inlet 213. The analyzer comprises a first detector 221 and a second detector 222.

[0083] A sample of process water, with an unknown concentration of frothing
25 agent, is drawn from a production plant and introduced to the mixing chamber 210 through the sample inlet 211, a first formulation is introduced to the mixing chamber 210 through the first formulation inlet 212, and a second formulation is introduced to the mixing chamber 210 through the second formulation inlet 213. The sample comprises a blend of frothing agents. The mixing chamber 210
30 facilitates the complexation or the reaction between the sample, and the frothing agents therein, with the formulations. The first formulation reacts, or complexes,

with one frothing agent to form a first modified frothing agent. The second formulation reacts, or complexes, with another frothing agent to form a second modified frothing agent. The detectable property of the first modified frothing agent is different to the detectable property of the second modified frothing agent. As such, the different detectable properties of the first and second modified frothing agents are measured separately. The mixing chamber 210 is connected to the analyzer 220 where the different detectable properties of the first and second modified frothing agents are measured by either the first detector 221 or the second detector 222. These measurements are compared to empirical data to determine the concentration of each frothing agent.

[0084] It will be appreciated that the mixing chamber 210 can comprise more than two formulation inlets and the analyzer 220 can comprise more than two detectors, so that the apparatus can be utilized to determine the concentration of multiple frothing agents.

[0085] As previously mentioned, the apparatus for determining the concentration of a frothing agent in a sample may further comprise a filter to remove insoluble particulate matter from the sample. The filter may be present in sample inlets 111 and 211. In this regard, insoluble particulate matter may clog the apparatus. As such, the removal of insoluble particulate matter may be advantageous. Additionally, the apparatus may also comprise a pretreatment for the sample to suppress the absorption of impurities such as collectors. In this regard, additional suppressants can be added to the sample prior to the formulation being mixed with the sample. Alternatively, the additional suppressant may be added to the formulation.

[0086] The detectors 221 or 222 can be used to measure different detectable properties of the same modified frothing agent. These different detectable properties can be combined to provide a more accurate determination of the concentration of a frothing agent. Alternatively, a single detector may be used to measure and quantify the detectable properties in two different modified frothing agents. In this regard, the detector may be able to detect absorbance simultaneously at two different wavelengths.

[0087] The apparatus is used as an online apparatus where the samples are automatically drawn from a line in a processing plant, automatically measured, automatically compared to empirical data, and the results automatically sent back to the system for optimization. To this end, a pump can be used to draw a sample from a line in the processing plant directly to the mixing chamber, and another pump can be used to draw a formulation from a formulation storage tank to the mixing chamber. The pump is suitably a peristaltic pump. The peristaltic pump controls the amount of sample and formulation that is drawn into the mixing chamber.

[0088] The formulation may be pre-made and stored in a formulation storage tank prior to its addition to the mixing chamber. It will be appreciated that each formulation inlet can be connected to multiple formulation storage tanks. Each formulation storage tank having a different formulation. The formulation inlet can then select the formulation to be automatically drawn to the mixing chamber based on the frothing agent in the sample.

[0089] It will also be appreciated that the formulation can also be prepared just prior to its addition to the mixing chamber. In this regard, the apparatus can further comprise a formulation mixing chamber that mixes the individual components of the formulation prior to its addition to the mixing chamber. The formulation mixing chamber can have multiple inlets for the individual components of the formulation, and facilitates the mixing of these components. This alleviates the problem with formulations that are unstable or cannot be stored. Additionally, this allows for many formulations to be prepared.

Examples

Example 1 - Sample formulation

[0090] A formulation was prepared containing the relative amounts of the components shown in Table 2 below. A stock solution of pyrene and a stock solution of β -cyclodextrin were prepared. The formulation was prepared by adding the desired amount of the stock solution of pyrene, the desired amount of the stock solution of β -cyclodextrin and deionized water to a vessel and mixing the contents until a homogeneous solution is formed. As pyrene is light sensitive

the formulation, and the stock solution of pyrene, was prepared and stored substantially in the absence of light.

Component	Amount
Pyrene	7×10^{-6} %.wt
β -cyclodextrin	0.5 %.wt
Deionized water	99.5 %.wt

Table 2 – Sample composition

Example 2 – Sample method of determining MIBC concentration

5 [0091] The concentration of MIBC, in a production line, was determined in a mineral processing plant by the following method. A metered amount of a sample was drawn from the production line. The sample was transferred to a mixing chamber where it was mixed with a stoichiometric excess of the formulation as described in Table 2. The resultant mixture was mixed for 1
10 minute and transferred to the analyzer where the absorbance at 340 nm was measured and compared to the MIBC calibration curve to determine the MIBC concentration.

Testing using process water from a coal mine

15 [0092] Tests were carried out with real process water samples from a coal mine in Central Queensland. This was completed to confirm the applicability of the technique in real samples obtained from processing plants.

[0093] Fine particulate matter, such as coal particles, from the sample was removed using a regenerated cellulose membrane with a pore size of 0.45 μm . In some tests, flocculants or salts were added to the sample to check its effect
20 on the present method with real process water.

[0094] In another set of tests, MIBC was added to test the applicability of the present method to analyze the frothing agent concentration in a flotation cell and in a water plant circuit. α -cyclodextrin was added to suppress the effect of diesel contaminants. The formulation was mixed with the samples at 180 rpm at 27°C
25 for 15 minutes before the UV-Vis absorbance was measured. Blank solutions

were made by using α -cyclodextrin in deionized water and mixing it with pyrene and β -cyclodextrin.

[0095] The addition of 3 ppm of flocculant or 0.03 M NaCl only had a minor influence on the measured Δ ABS values. This is consistent with the previous findings that inorganic electrolytes and/or flocculants had little impact on the frothing agent concentration measurement. These results are shown in FIG 15.

[0096] As previously mentioned, α -cyclodextrin was added to suppress the effect of diesel contaminants. In this regard, 5×10^{-5} M and 5×10^{-4} M of α -cyclodextrin was added to see its effect on the absorbance. The results are shown in FIG 16. The gradient of the curve was similar to that obtained using deionized water, which supports the high sensitive of the present method with real plant water. In addition, it was noted that a 10-fold increase in α -cyclodextrin had little impact on the Δ ABS. As such, this provides flexibility in developing the formulation to cope with situations where the concentration of diesel is not known. In other words, it is possible to add an excess of α -cyclodextrin to ensure that residual diesel is suppressed, even if the diesel concentration is unknown.

[0097] The above description of various embodiments of the present invention is provided for purposes of description to one of ordinary skill in the related art. It is not intended to be exhaustive or to limit the invention to a single disclosed embodiment. As mentioned above, numerous alternatives and variations to the present invention will be apparent to those skilled in the art of the above teaching. Accordingly, while some alternative embodiments have been discussed specifically, other embodiments will be apparent or relatively easily developed by those of ordinary skill in the art. Accordingly, this invention is intended to embrace all alternatives, modifications and variations of the present invention that have been discussed herein, and other embodiments that fall within the spirit and scope of the above described invention.

CLAIMS

1. An automated method for determining the concentration of a frothing agent in a sample comprising the steps:

5 a. drawing a sample with an unknown concentration of frothing agent from a line in a production plant;

b. adding a formulation to the sample;

c. mixing the sample and the formulation to form a modified frothing agent having a detectable property;

d. measuring and quantifying the detectable property; and

10 e. comparing a measured detectable property of the modified frothing agent with a database of known empirical data to determine the concentration of the frothing agent in the sample.

15 2. An apparatus for determining the concentration of a frothing agent in a sample comprising:

a mixing chamber having a sample inlet and at least one formulation inlet; and

an analyser connected to the mixing chamber, the analyser having at least one detector that measures at least one detectable property;

20 wherein a sample is drawn from a line in a production plant and introduced to the mixing chamber through the sample inlet and a formulation is introduced to the mixing chamber through the at least one formulation inlet, and wherein the formulation and the frothing agent form a modified frothing agent that exhibits the detectable property.

25 3. The method of claim 1, or the apparatus of claim 2, wherein the frothing agent is an alcohols or a glycol.

4. The method of claim 1, or the apparatus of claim 2, wherein the frothing agent is selected from the group consisting of 4-methylpentan-2-ol

(MIBC), 4-Methylcyclohexanemethanol (MCHM) and 1-(2-methoxy-1-methylethoxy)propan-2-ol (DowFroth250).

5. The method of claim 1, or the apparatus of claim 2, wherein the formulation comprises one or more components selected from the group consisting of polyaromatic hydrocarbons, compounds with a cavity to accommodate a frothing agent, indicators and solvents.

6. The method or the apparatus of claim 5, wherein the polyaromatic hydrocarbon is pyrene.

7. The method or the apparatus of claim 5, wherein the compound with a cavity to accommodate a frothing agent is β -cyclodextrin.

8. The method or the apparatus of claim 5, wherein the indicator is selected from the group consisting of phenolphthalein, crystal violet, and congo red.

9. The method or the apparatus of claim 5, wherein the solvent is selected from the group consisting of water and alkyl alcohol.

10. The method of claim 1, or the apparatus of claim 2, wherein the detectable property is selected from the group consisting of conductivity and optical properties.

11. The method of claim 1, or the apparatus of claim 2, wherein the formulation comprises pyrene, β -cyclodextrin and water.

12. The method of claim 1, or the apparatus of claim 2, wherein the formulation comprises pyrene, β -cyclodextrin, water and methanol.

13. The method of claim 1, or the apparatus of claim 2, wherein the formulation comprises pyrene, β -cyclodextrin and methanol.

14. The method of claim 1, or the apparatus of claim 2, wherein the formulation comprises phenolphthalein, β -cyclodextrin and deionized water.

15. The method of claim 1, or the apparatus of claim 2, wherein the modified frothing agent is formed within 15 minutes.

16. The method of claim 1, or the apparatus of claim 2, wherein the detectable property is selected from the group consisting of electrochemical properties and optical properties.

17. The method of claim 1, or the apparatus of claim 2, wherein the formulation further comprises a suppressant.

18. The method of claim 1, wherein the method has a measuring accuracy of less than 2 ppm.

19. The apparatus of claim 2, wherein the sample inlet comprises a filter.

20. The apparatus of claim 2, wherein the detector is an electrochemical detector or an optical detector.

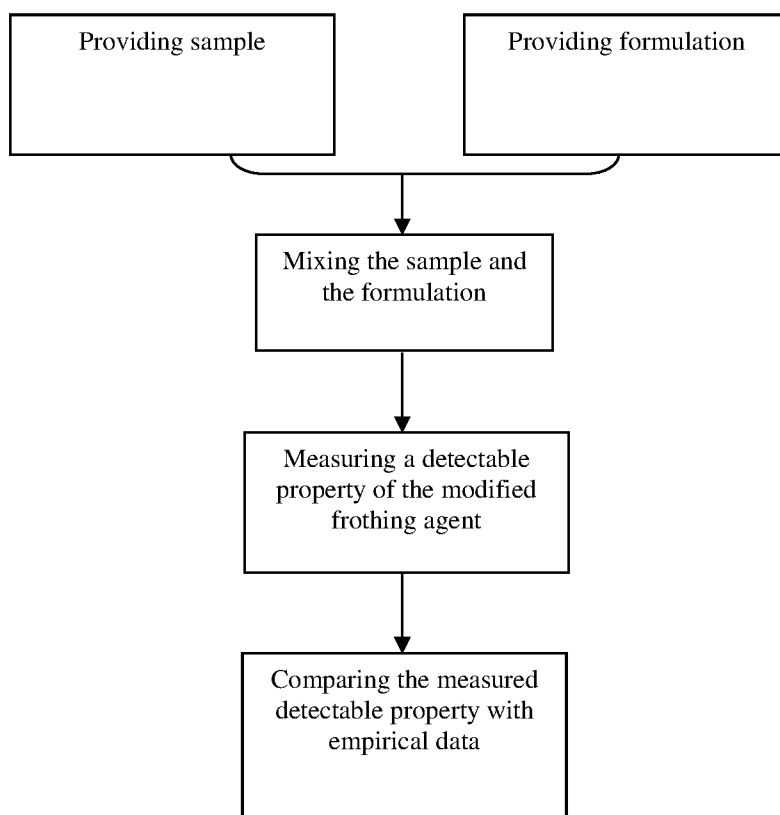


FIG 1

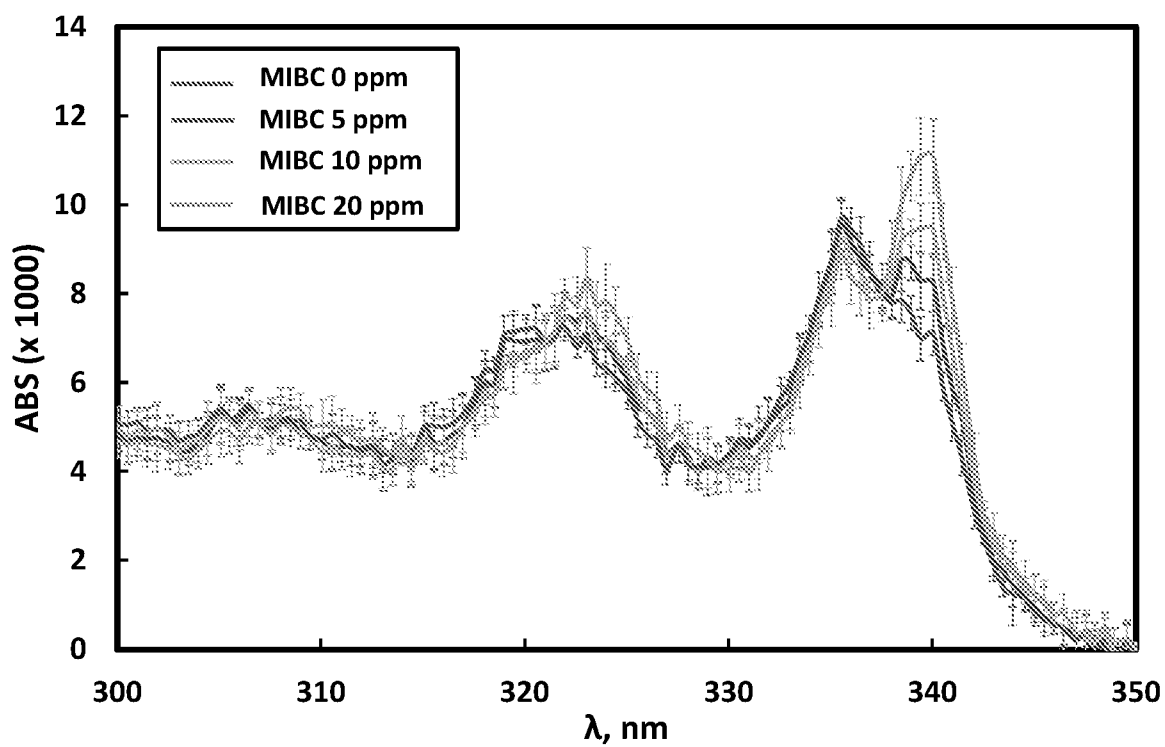


FIG 2

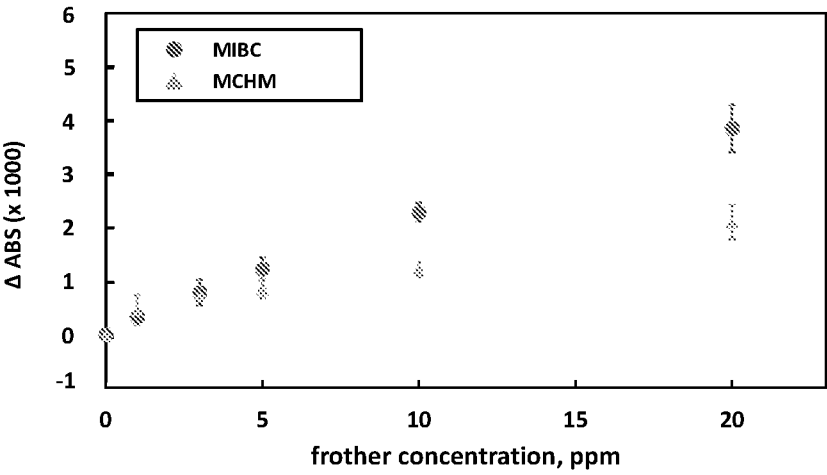


FIG 3

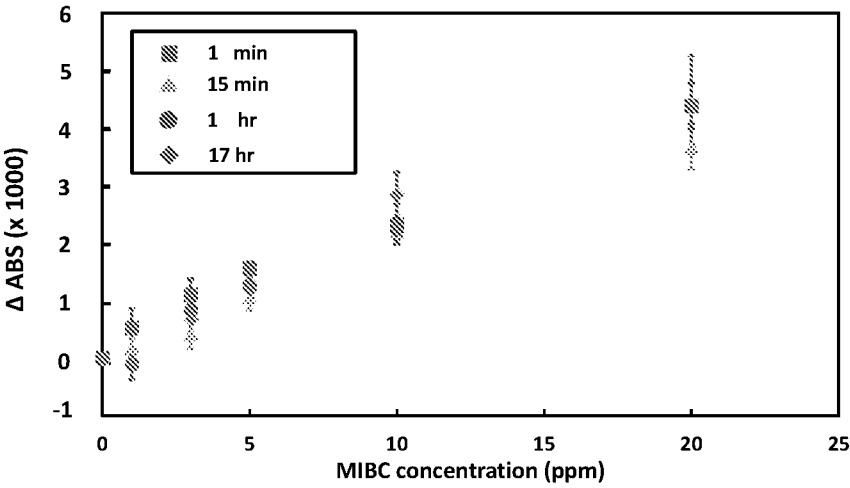


FIG 4

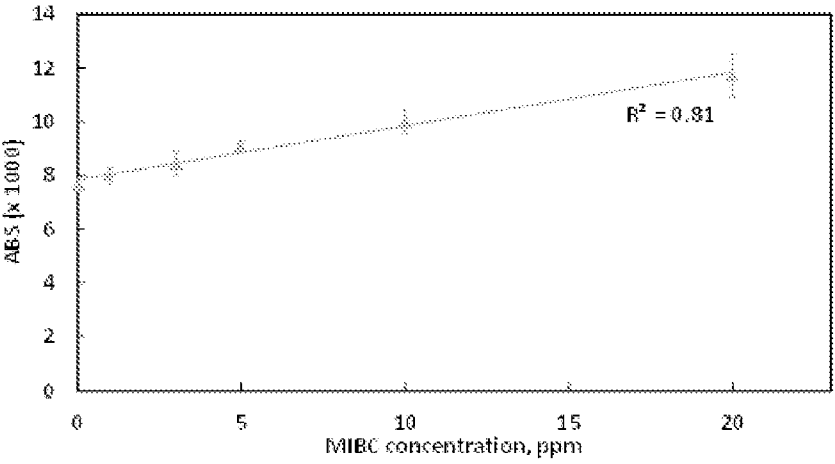


FIG 5a

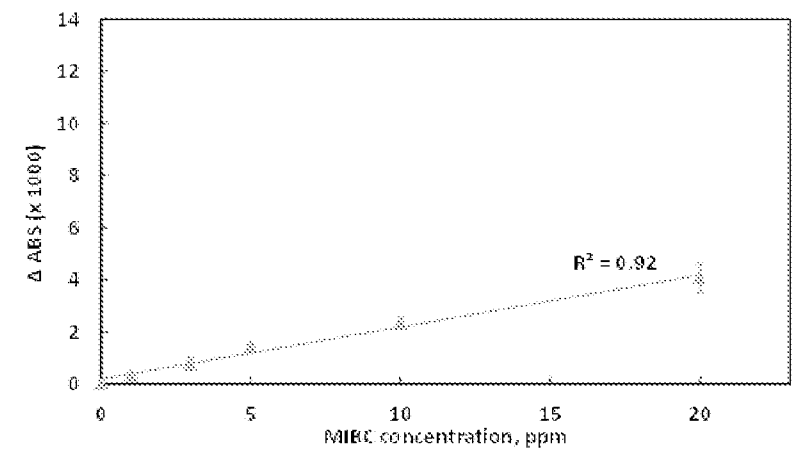


FIG 5b

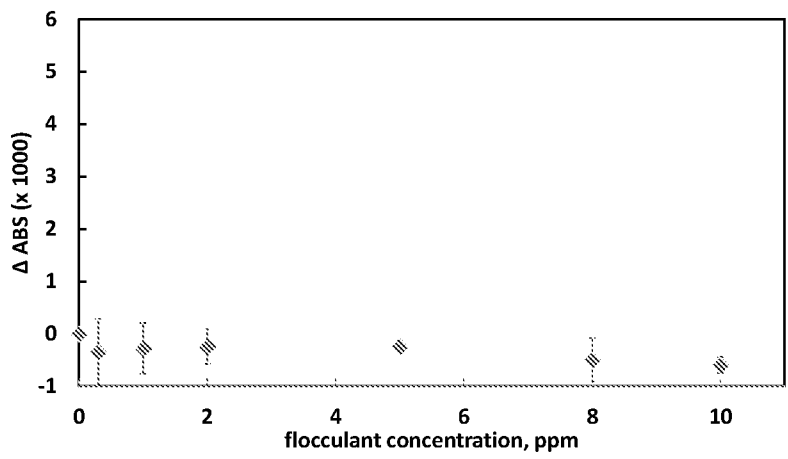


FIG 6

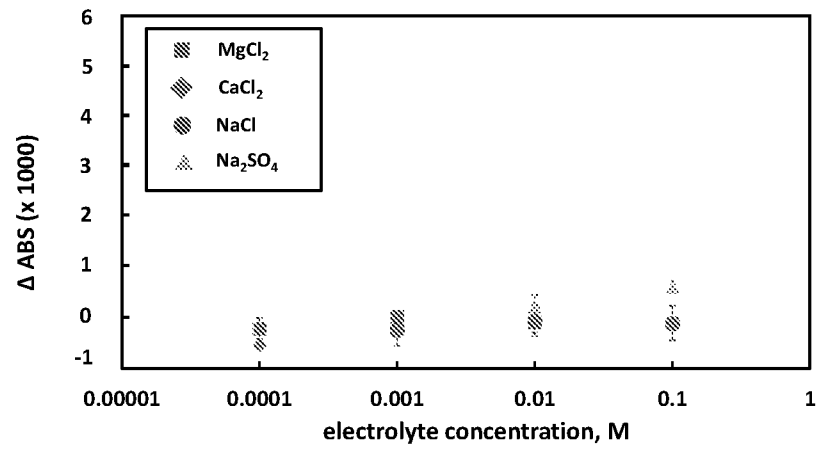
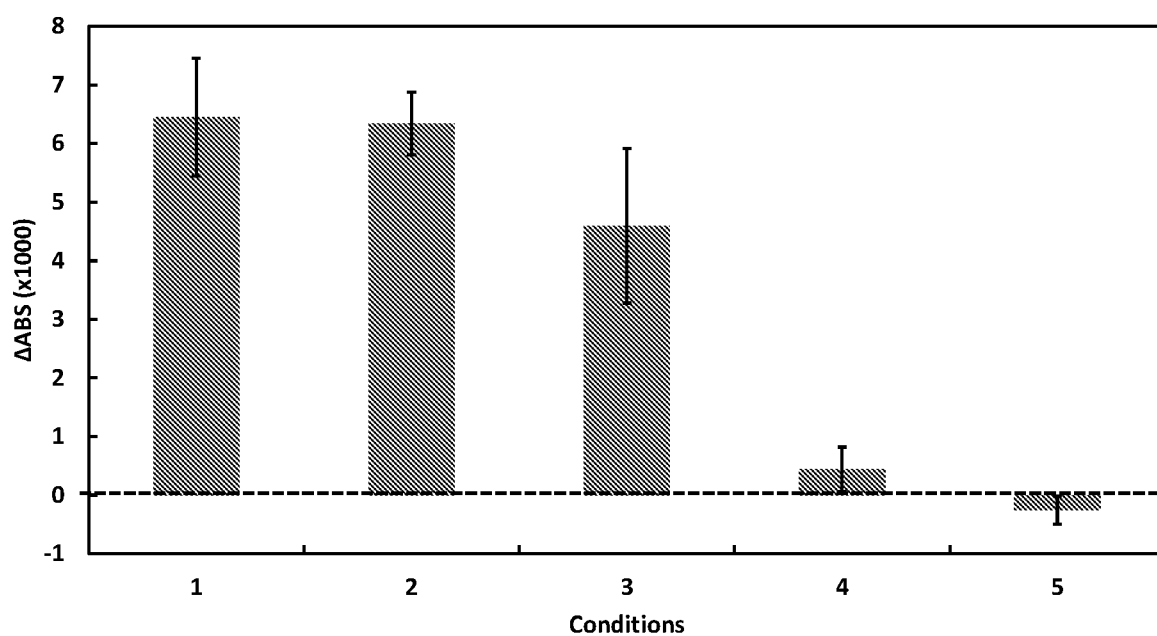


FIG 7



Condition 1: pyrene (0.34 μM) + β -CD (4.2 mM) + diesel (0.8 ppm).

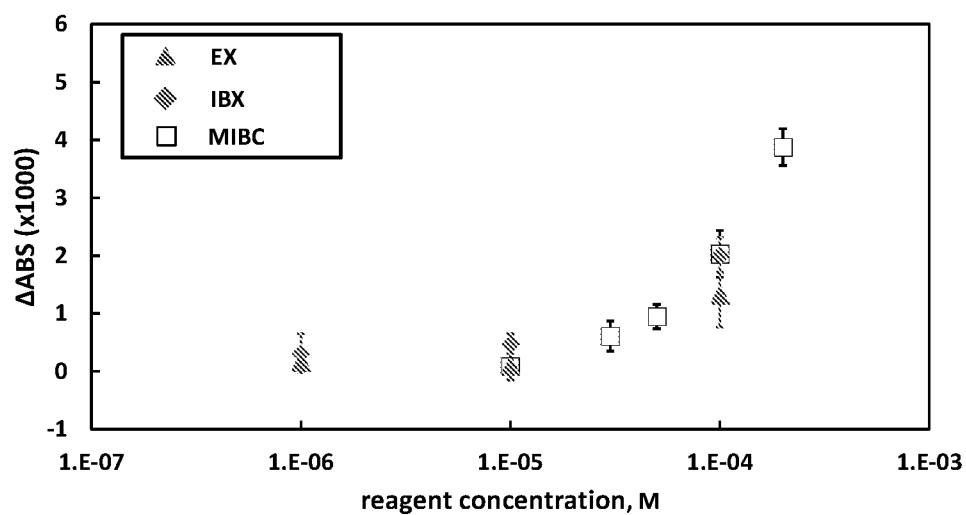
Condition 2: pyrene (0.34 μM) + β -CD (4.2 mM) + diesel (0.8 ppm) + α -CD(10^{-5} M).

Condition 3: pyrene (0.34 μM) + β -CD (4.2 mM) + diesel (0.8 ppm) + α -CD(10^{-4} M).

Condition 4: pyrene (0.34 μM) + β -CD (4.2 mM) with pre-added mixture of diesel (0.8 ppm) and α -CD(10^{-5} M).

Condition 5: pyrene (0.34 μM) + β -CD (4.2 mM) with pre-added mixture of diesel (0.8 ppm) and α -CD(10^{-4} M).

FIG 8



EX: ethyl xanthate;

IBX: sodium isobutyl xanthate;

MIBC: 4-methyl-2-pentanol.

FIG 9

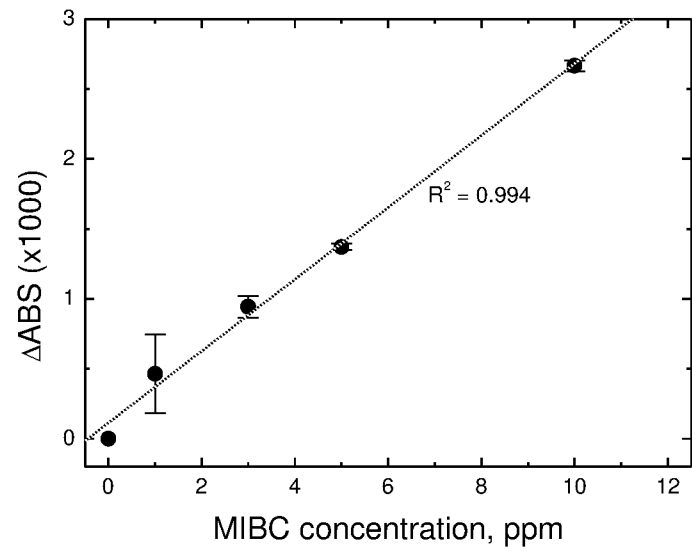


FIG 10

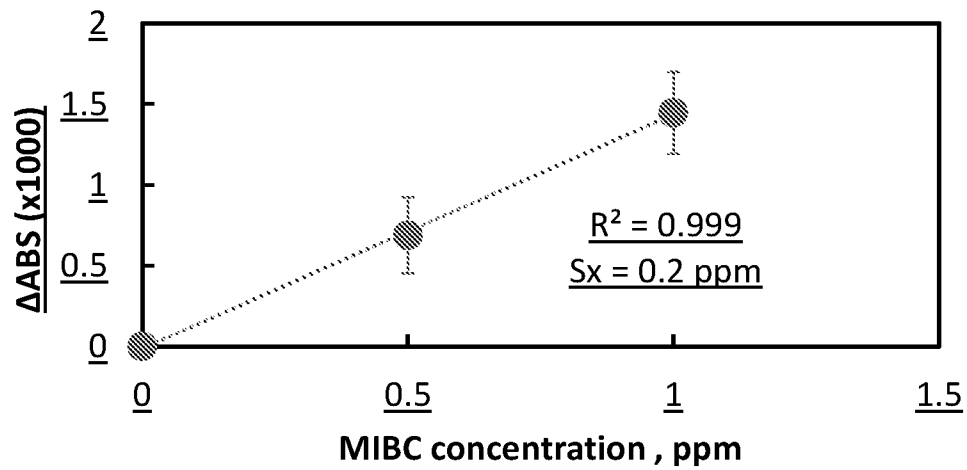


FIG 11

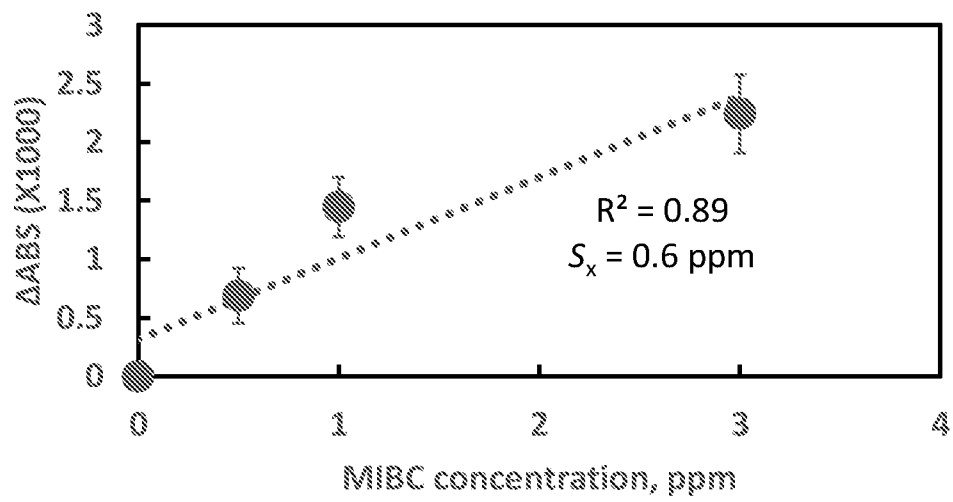


FIG 12

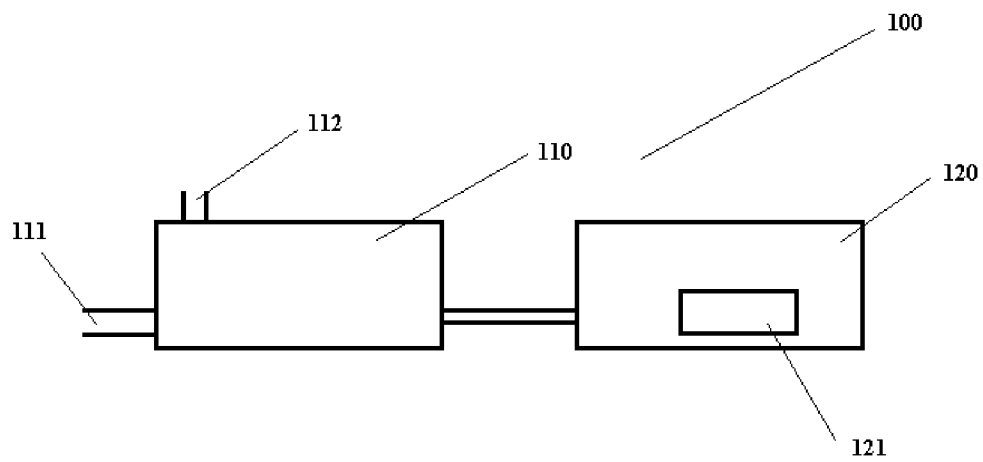


FIG 13

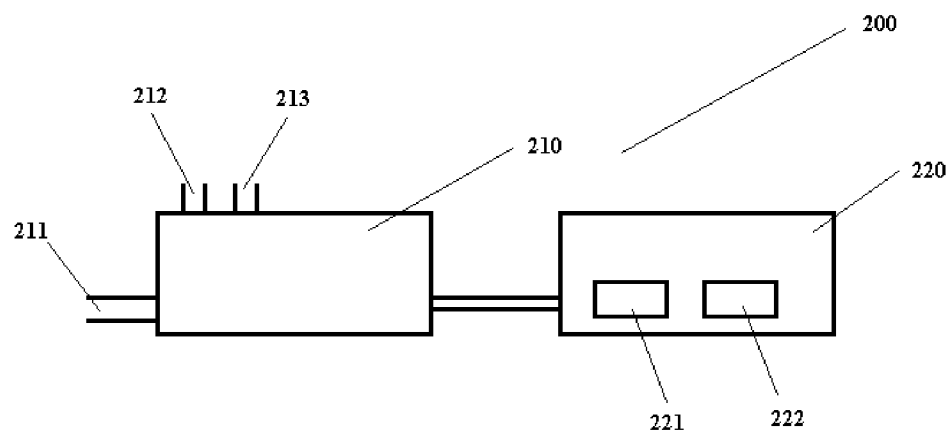


FIG 14

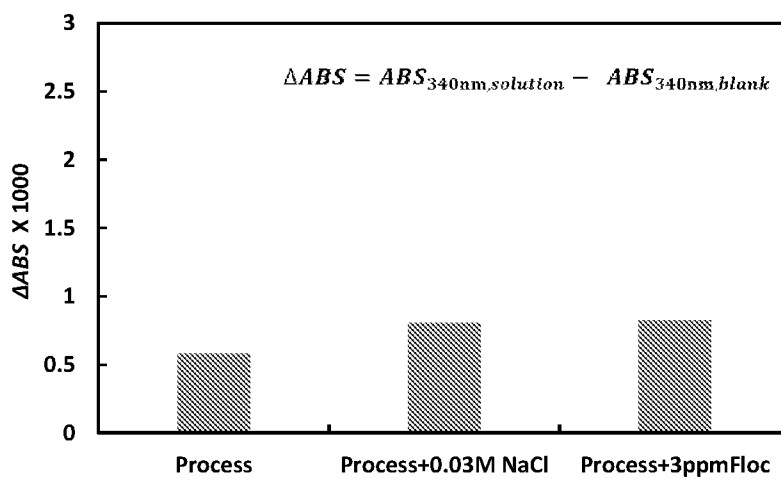


FIG 15

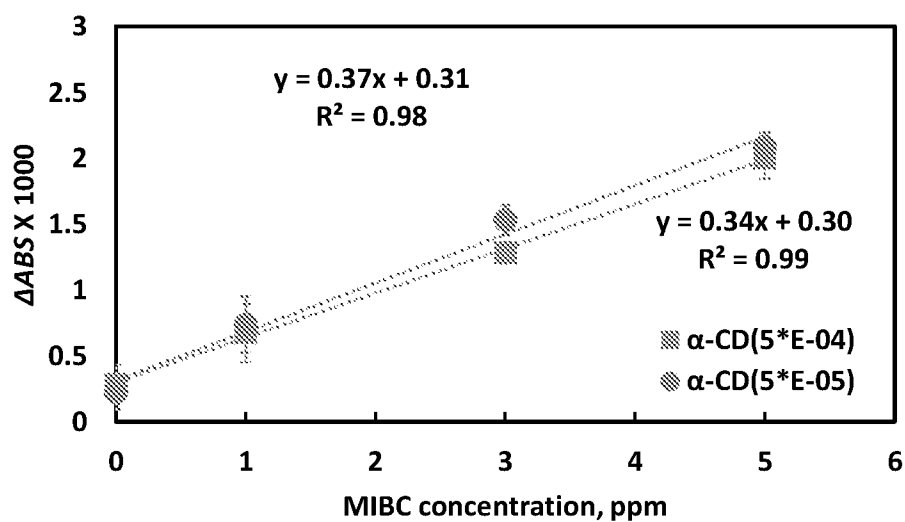


FIG 16

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2017/050008

A. CLASSIFICATION OF SUBJECT MATTER

B03D 1/00 (2006.01) G01N 21/25 (2006.01) G01N 21/64 (2006.01) C09B 13/00 (2006.01) C08L 5/16 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

 Databases: PATENW in Logical databases (WPI, EPODOC, Full text), IPC/CPC marks: B03D1/00, G01N21/00, C09B13/00, C08L5/16, and keywords: calculate, measure, analyse, monitor, detecting, froth, alcohol, glycol, electro-chemical, conductivity, optical, spectroscopy, hydrocarbons, pyrene, cyclodextrin, comparing, databases, library and similar terms.
 Applicant(s)/Inventor(s) name searched in internal databases provided by IP Australia.

Applicant(s)/Inventor(s) name search in Espacenet, AusPat, Google Patents/Google scholar: Applicant name: The University of Queensland; Inventor name: Park, Hangil; Wang, Liguang, keywords: minerals, froth, modifying agent, concentration, pyrene, aromatic hydrocarbons, cyclodextrin, electro chemical, optical, spectroscopy, fluorescence, spectra, and similar terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

 Date of the actual completion of the international search
 19 May 2017

 Date of mailing of the international search report
 19 May 2017

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 Telephone No. 0262223654

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2017/050008
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2952259 A1 (ABB Research Ltd.) 09 December 2015 paragraphs 0011, 0019, Fig. 1 and paragraphs 0068-0079	1-20
X	WO 2009/066167 A2 (UNIVERSIDADE FEDERAL DE MINAS GERAISUFMG) 28 May 2009 page 5, lines 3-25, Examples 1-2	1-20
Form PCT/ISA/210 (fifth sheet) (July 2009)		

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2017/050008	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
EP 2952259 A1	09 December 2015	EP 2952259 A1	09 Dec 2015
		AU 2015270654 A1	02 Feb 2017
		CN 106537119 A	22 Mar 2017
		EP 3151969 A2	12 Apr 2017
		WO 2015185488 A2	10 Dec 2015
WO 2009/066167 A2	28 May 2009	WO 2009066167 A2	28 May 2009
		BR PI0705593 A2	21 Jul 2009
		BR PI0705593 B1	12 Apr 2016
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			