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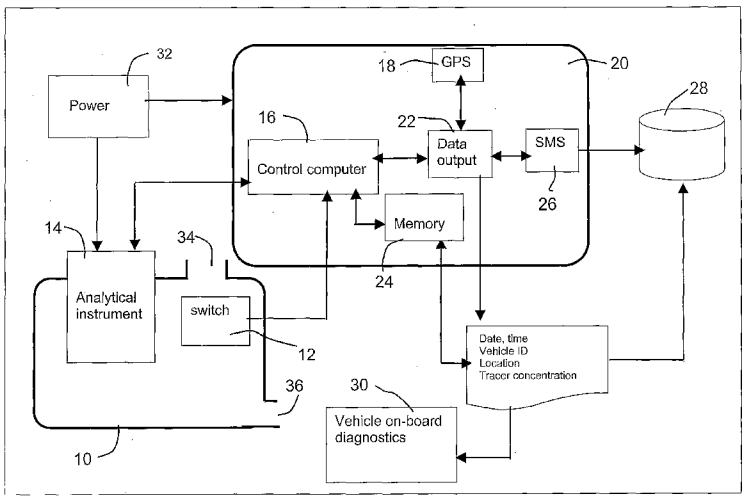

(57) Abstract: A system for the verification of an aqueous urea solution suitable for use in a process for the selective catalytic reduction of nitrogen oxides emitted from a diesel engine mounted in a vehicle, said aqueous urea solution comprising from 30 - 35% of urea comprises a) a tracer composition comprising a first tracer compound, optionally at least one secondary tracer compound and optionally a solvent, the tracer composition being soluble in said aqueous urea solution b) analytical apparatus adapted to measure the concentration of said first tracer compound in a sample of said urea solution and compare said concentration with the concentration of tracer in a standard sample of urea solution containing a pre-determined amount of said first tracer compound said analytical apparatus being mounted on or within said vehicle, and c) an indicating means for indicating when the difference between the concentration of said first tracer in the urea solution and the concentration of tracer in the standard sample of the urea solution exceeds a pre-determined value.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Tagging system

The present invention relates to a tagging method for use in tagging an aqueous liquid, particularly a urea solution for use in selective catalytic reduction systems used to treat exhaust emissions, particularly exhausts from diesel engines.

Heavy-duty diesel engines which are used largely in commercial vehicles are subject to increasing regulation of emission levels. It is therefore important to provide such engines with measures to reduce harmful emissions, especially particulates, and nitrogen oxides (NO_x). Selective catalytic reduction (SCR) is a technology which has been introduced to reduce emissions of NOx by chemically reducing the NOx to nitrogen. Ammonia-SCR systems react ammonia (NH_3) with the NOx to form nitrogen (N_2) and water (H_2O). There are three reaction pathways:

$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$

$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$

$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$

Any source of ammonia can be used but most commonly the source is an aqueous solution of urea. This decomposes in the exhaust stream in two stages to form ammonia and carbon dioxide. The commercial standard form of urea sold for this purpose in Europe is a 32.5% aqueous urea solution, known as AUS 32 (Aqueous Urea Solution) and by the trade name AdBlue™, which conforms to ISO 22241-1:2006 and DIN 70070 standard for urea solution for use in SCR systems.

A concern with the introduction of such an additive is the control and monitoring of the use of suitable quality product which conforms to the accepted regulatory standard. With the introduction of mandatory emission control measures in many countries, the use of SCR technology will become regulated and therefore liable to inspection. Dilution of conforming AdBlue or the use of AdBlue from a non-conforming source should be capable of being monitored by representatives of appropriate regulatory bodies and others having an interest in monitoring and maintaining the quality of the urea solution used. This is most obviously for the purpose of ensuring that vehicle emissions of NOx using SCR technology are suitably controlled, but also to ensure that the correct grade of urea solution is used to avoid the poisoning of the SCR catalyst and to protect urea product branding for commercial purposes. It is an object of the present invention to provide a tagging system for urea solutions for use in SCR systems and to provide a method of tagging urea and determining the source of a urea solution.

According to the invention we provide a system for the verification of an aqueous liquid, the system comprising

a) a tracer composition comprising a first tracer compound, optionally at least one secondary tracer compound and optionally a solvent, the tracer composition being soluble in said aqueous liquid

b) analytical apparatus adapted to measure a property of a target sample of said liquid, which property varies according to the concentration of said first tracer compound in the solution, and compare said measured property with the same property measured for a standard sample of the liquid containing a pre-determined amount of said first tracer compound

said analytical apparatus being mounted on or within said vehicle, and

c) an indicating means for indicating when the difference between the property measured for the target sample of the liquid and the property of the standard sample of the liquid exceeds a pre-determined value.

Preferably the aqueous liquid comprises a urea solution suitable for use in a process for the selective catalytic reduction of nitrogen oxides emitted from a diesel engine mounted in a vehicle, said aqueous urea solution most preferably comprising from 30 – 35% by weight of urea.

In a preferred embodiment of the invention, the verification system comprises:

(i) a tracer composition comprising at least one tracer compound capable of absorbing radiation of a wavelength in the range 200 – 1100nm,

and

(ii) a portable analytical apparatus mounted on or within a vehicle, comprising

a) a source of excitation radiation, adapted to irradiate a target sample of the aqueous liquid with light at a predetermined wavelength, said predetermined wavelength being selected to be capable of being absorbed by at least one of said tracer compounds,

b) a radiation detector arranged to detect radiation emitted from or transmitted by the target sample,

c) a data collection and manipulation device for gathering data from the radiation detector and producing information concerning the intensity and wavelength of the emitted or transmitted radiation detected by the radiation detector,

d) data-processing means for comparing the characteristics of intensity and wavelength of the light emitted from or transmitted by the target sample when irradiated by said radiation source with the characteristics of radiation emitted from or transmitted by a standard sample containing a predetermined concentration of the tracer compound, and

e) indication means to indicate whether the characteristics of the light emitted from or transmitted by the target sample are within a predetermined range of the characteristics

The invention further comprises an analytical apparatus comprising

a) a source of radiation, adapted to irradiate a target sample of an aqueous liquid with light at a predetermined wavelength, said predetermined wavelength being selected to be capable of being absorbed by at least one of said tracer compounds,

b) a radiation detector arranged to detect radiation emitted from or transmitted by the target sample,

c) a data collection and manipulation device for gathering data from the radiation detector and producing information concerning the intensity and wavelength of the emitted or transmitted radiation detected by the radiation detector and data-processing means for comparing the characteristics of intensity and wavelength of the light emitted from or transmitted by the sample when sample is irradiated by said radiation source with the characteristics of radiation emitted from a standard sample of the liquid containing a known quantity of the tracer compound, and

d) indication means to indicate whether the characteristics of the light emitted from or transmitted by the sample are within a predetermined range of the characteristics of the light emitted from or transmitted by the standard sample

characterised in that the radiation source and detector are mounted on or within a vehicle and are adapted to irradiate and detect radiation emitted from or transmitted by a sample of a urea solution used in a selective catalytic reduction process for treating emissions from the engine of a vehicle.

The invention further comprises a vehicle having a diesel engine, a selective catalytic reduction apparatus for treating the gaseous emissions from said engine, and a container for containing an aqueous urea solution for use in the selective catalytic reduction apparatus, characterised in that said vehicle further comprises an analytical apparatus adapted to measure a characteristic property of a tracer compound, the analytical apparatus being located to analyse a sample of the aqueous urea solution within said container or within a conduit associated with said container.

The invention further comprises a method of characterising a urea solution used in a selective catalytic reduction process for treating emissions from the engine of a vehicle, by comparison with a reference standard sample of a urea solution containing a pre-determined amount of a tracer compound, comprising analysing a target sample of said urea solution to measure a characteristic property of said tracer compound in said sample and comparing the measured property with the property measured by analysing said reference standard sample of a urea solution, characterised in that the analysis of the urea solution and the comparison of the measured characteristic property of the target sample of urea solution with that of the reference standard sample is performed using analytical apparatus mounted on or within said vehicle

The urea solution preferably comprises a 32.5% aqueous solution of urea in accordance with the ISO 22241-1:2006 & DIN 70070 standard for urea solutions for SCR systems to reduce emissions of nitrogen oxides from diesel engines, known commercially as AdBlue®. The standard allows a urea content of from 31.8 – 33.2%.

Target sample in this specification refers to a sample of liquid in which the amount of tracer is unknown or is desired to be verified. The target sample may be isolated from a bulk of an unknown liquid or may comprise a portion of a bulk of liquid contained in a vessel or flowing through a pipeline on the vehicle. The target sample may contain none of the tracer compound, depending on its source. Using the method, apparatus and system of the invention it is intended to provide a means of ascertaining whether the target sample contains any tracer at all and if present, its relative concentration compared with a reference sample. The reference sample is a sample of the liquid containing a known amount of the tracer compound, which is preferably the amount of tracer contained in authorised samples of the liquid released into the supply chain. The reference sample need not be measured on the vehicle or contemporaneously with target sample measurement. The reference sample may be represented by data held by the analytical apparatus or data-processor obtained from an earlier measurement taken ex-situ.

By verification system, we mean a combination of a compound and apparatus suitable for ascertaining that liquid, e.g. a urea solution measured by the measurement apparatus is substantially the same as an approved urea solution in accordance with a relevant standard to which the tracer compound has been added. This is achieved in the present invention by comparing a characteristic property of a standard reference solution containing a predetermined concentration of tracer compound with the same property measured for a target sample of the liquid, the measurement and comparison being carried out using apparatus mounted on or in a vehicle in which the liquid is intended to be used, e.g. for which the target urea solution is to be used in an SCR apparatus on that vehicle. The characteristic property measured varies according to the concentration of a tracer compound in the solution. In this way it is possible to determine whether the target liquid sampled contains substantially the same concentration of a tracer compound as the reference sample of liquid to which the known predetermined amount of tracer composition was added and thus whether the solution may have been diluted or substituted with a different solution. It is not necessary to calculate the concentration of tracer compound in the sample from the value of the measured property but it is within the scope of the invention to do so if convenient. When the liquid, is for distribution through a supply chain and it is required to be traced through the distribution channels, the tracer is added prior to distribution. Normally the tracer composition is added to the liquid during its manufacture. When the liquid is AdBlue, the tracer is preferably added prior to the distribution of the liquid by the manufacturer to wholesale and retail outlets, e.g. fuel suppliers and forecourts.

The tracer composition may be a liquid or a solid but it must be soluble in or substantially completely miscible with the liquid. The concentration of the tracer compound in the aqueous liquid is preferably in the range from 1 ppb - 20 ppm w/v, more preferably from 10 ppb to 10 ppm, especially from 10 ppb – 1 ppm.

The chemical nature of the tracer compound selected for use in the system and method of the invention is dependent upon the analytical method and apparatus selected, and vice versa, i.e. for use in verification of a urea solution an analytical method and suitable tracer analyte is selected to be adapted for installation and use in or on a vehicle and for the tracer to be compatible with the urea solution. The tracer composition must not contain components which are likely to be unstable in the urea solution or otherwise change their characteristics on storage in the urea solution. Furthermore the use of tracer compounds which can poison the SCR catalyst or which are likely to decompose into compounds which poison or are incompatible with the catalyst or other parts of the exhaust system should be avoided. ISO 22241-1:2006 lists the required quality characteristics for AUS 32 including maximum limits for the content of various metals and other chemicals in the solution. The urea solution including the tracer compound should conform to the listed quality characteristics of this standard.

In a preferred embodiment, the tracer compound may be a fluorescent compound, i.e. a compound which, when irradiated with light at or near its excitation wavelength (excitation radiation) emits fluorescent radiation at a characteristic emission wavelength which is different from the excitation wavelength. The fluorescent compound is preferably activated by radiation in the ultra-violet or infra red portions of the spectrum and preferably is excited by radiation of a wavelength in the range from 200 - 1100 nm , more preferably 250 – 700 nm and emits fluorescent radiation at a wavelength in the range from 300 – 1200 nm, more preferably 300 – 800 nm. Alternatively the tracer compound may be a non-fluorescent radiation absorbing compound, detectable by shining radiation, preferably of a wavelength in the range from 200 - 1100 nm through a sample of the liquid and measuring the amount of radiation transmitted by the sample at a single wavelength or band of wavelengths. The wavelengths measured are selected to include one or more wavelengths or bands of wavelengths at which the tracer compound is known to absorb light and preferably at which the absorption is characteristic for the tracer compound.

In a preferred embodiment of the system, where the tracer compound is a fluorescent compound, the amount of tracer compound is measured using an emission spectrometer, in particular a portable fluorimeter which is mounted upon or within a vehicle having a vessel for containing the liquid, e.g. an aqueous urea solution for use in a SCR system for the treatment of exhaust gases from said vehicle. The concentration of tracer compound in the urea solution is measured in-situ

through which the aqueous liquid flows as it is filled into the vessel or through which the urea solution passes to the SCR system. In such an arrangement the measurement apparatus may comprise a probe having a source of excitation radiation arranged to irradiate a space within the probe, the space being adapted to receive a liquid sample, and a detector for detecting fluorescent radiation emitted from a liquid sample contained within the space. Such probes are known for the in-situ spectroscopic measurement of liquids. Alternatively the light source and detector may be arranged to irradiate and measure fluorescence emitted from or transmitted by a liquid flowing through a conduit located within the vehicle. In this form the conduit preferably includes a portion which is transparent to the excitation and emission/ transmission wavelengths of the tracer compound, e.g. the conduit may comprise a UV- or IR- transparent portion. When the detector is adapted to detect fluorescence emitted from a fluorescent tracer compound, it is located out of the path of the excitation radiation.

In a suitable portable instrument for the detection of the tracer compound by measurement of radiation emission or absorption, the excitation radiation source may comprise any suitable source including a full-spectrum light source with a suitable band-pass filter or, more preferably, by a single or narrow-band source. Suitable sources include a deuterium lamp filled with a narrow band-pass filter, a light emitting diode (LED) or die array or a laser source. Laser light sources are available at many different wavelengths and may be selected or tuned to provide light of the correct wavelength to excite fluorescence in the fluorescent materials. It is preferred to provide a separate source for each fluorescent tracer compound present in the sample, each source being selected and tuned or filtered to emit radiation at or near the frequency of maximum absorption of a respective tracer compound. In order to provide for simple portability of the apparatus, solid laser diode sources are preferred to dye lasers, or a xenon lamp having a suitable filter or monochromator. LEDs are an alternative preferred radiation source. LEDs are available which emit radiation over a wide band of wavelengths or within a narrower band of wavelengths. The radiation emitted by the light source may be filtered to provide excitation radiation of the selected wavelength or within the selected band of wavelengths.

The detector for detecting the emitted fluorescent radiation or transmitted radiation may be selected from a variety of known detector types. Suitable detectors include a photomultiplier tube or photodiode having a suitable cut-off filter, monochromator or band-pass filter adapted to pass wavelengths at or near the desired fluorescent wavelength of the tracer compound. Alternatively a charge coupled device is a convenient form of detector, particularly adapted for a portable fluorescence measurement device. A plurality of detectors may be used, particularly where more than one tracer compound is used in the tracer composition. In this form, it is convenient to provide a detector adapted to detect the fluorescent radiation emitted from each single tracer compound. The analytical instrument preferably comprises a data processor and/or control

example, when more than one light source is present, means are provided to indicate to the data-processor which radiation source is being used and to control the synchronisation of the light sources and detector(s).

The fluorescent compound used in a preferred embodiment of the system is selected to be soluble in and compatible with aqueous urea solution. Most preferably the tracer compound fluoresces at a peak wavelength which is distinguishable from the fluorescence of the non-tracer components of the solution, when irradiated with light at a wavelength capable of exciting fluorescence in the fluorescent tracer compound. The tracer composition may include more than one fluorescent tracer compound. If the apparatus provides sufficient spectral resolution and the excitation and emission wavelengths do not interfere with each other then the concentration of several fluorophores may be measured simultaneously. The amount of fluorescent tracer compound in a sample of the solution is determined by measuring the fluorescent radiation emitted from the sample when it is irradiated with light of a wavelength which excites fluorescence within the tracer compound.

The excitation wavelength selected depends upon the shape of the absorption peak of the particular fluorescent compound used as a tracer. The excitation wavelength may be a range of wavelengths within which the dye is stimulated to fluoresce. The excitation wavelength is preferably less than or about equal to the wavelength of maximum absorption in order to avoid detection of the excitation radiation and interference with the fluorescence emission spectrum. Preferably the wavelength of excitation is within the range between λ_P and λ_{-2} where λ_P is the wavelength of the maximum absorption, i.e. the peak wavelength, and λ_{-2} is the minimum wavelength at the full width at 20% of the peak height of the absorption peak of the dye. When the wavelength of excitation is shorter than this, the dye may still be excited but the response to the excitation radiation may be less because less energy is absorbed by the dye. More preferably, the wavelength of excitation is within the range between λ_P and λ_{-5} where λ_{-5} is the minimum wavelength at the full width half peak height of the absorption peak of the dye. More preferably the excitation wavelength is within the range between λ_P and λ_{-9} where λ_{-9} is the minimum wavelength at the full width nine tenths height of the absorption peak of the dye. Normally the excitation radiation is selected to be within about 30nm of the wavelength of maximum absorption of the dye which is to be detected. The wavelength of maximum absorption, and the fluorescent emission wavelength is normally known and documented for commercial dyes. In case these parameters are not known, it is a matter of routine to measure the spectral absorption and emission for a particular dye using standard spectrometry apparatus.

Suitable tracer compounds include many commercial fluorescent dyes known in the art of tracers and include, for example, xanthenes, phthalocyanines, naphthalocyanines, nickel-dithiolane

coumarins, pyrromethenes, alkylated dibenzanthrone, anthraquinones, squarines, rhodamines and oxazines, amongst others. For use in tagging aqueous urea solution for SCR systems, some dyes in the form of metal salts should be avoided in order to be compatible with the requirements of the urea solution according to the international standard.

An alternative preferred tracer compound comprises a radiation absorbing compound. Any soluble compound which absorbs radiation in a part of the spectrum from the ultraviolet to the infra red regions is suitable and, of course, such compounds include fluorescent compounds as described hereinbefore. In this case, the apparatus for measuring the concentration of the tracer compound may therefore comprise an absorption spectrometer comprising a radiation source arranged to shine light through a sample of the urea solution and a detector which is adapted to measure the radiation from the source which is transmitted by the urea solution. When the tracer compound has a known characteristic radiation absorption spectrum, it may be identified and quantified in a sample of the urea solution by comparing the absorption spectrum, or a specific portion of the spectrum, obtained from the sample with the spectrum obtained from a sample containing a known amount of the tracer compound. Suitable source and detector apparatus has already been described in relation to fluorescence measurement.

As a further alternative, the tracer compound may comprise one or more of a variety of organic molecules such as alcohols, including phenols and halogenated alcohols, organic acids, optionally containing halogen atoms, and carbohydrates (sugars). Suitable analytical methods may include ion-mobility spectrometry (IMS), particularly miniaturised or micro-IMS which is particularly suitable for the detection of trace amounts of compounds. Other analytical apparatus and methods which may be used on the vehicle include those using surface acoustic waveform (SAW) methods or amplifying fluorescent polymeric (AFP) sensors. Other methods such as mass-spectrometry may also be suitable if the relevant apparatus can be made sufficiently small and robust for use on a vehicle. Advances in the field of microengineered measurement systems, analytical apparatus and detectors may make other types of detectors suitable for use in the current method and system. A combination of analytical apparatus and detection methods may be provided.

The apparatus may comprise means for identifying the presence of more than one tracer compound. This may be required if the tracer composition added to the urea is different according to the source of urea or the region in which the urea is purchased. The means for identifying the presence of more than one tracer compound may comprise more than one source and/or detector each of which is adapted to emit or detect radiation of a specified wavelength or band of wavelengths. The means may alternatively comprise at least one source or detector which is capable of emitting or detecting radiation of more than one selected wavelength or band of wavelengths. The wavelengths are selected to match the excitation/emission or absorption

The measurement apparatus further comprises indication means by which the measured emitted fluorescent radiation is indicated. The indication means may comprise a display such as a graphical or numerical indication of the measured radiation at the emission wavelength of the fluorescent compound. Such a display may simply comprise a light or indication of whether the emitted radiation is within or outside of pre-determined parameters, calculated to indicate whether the measured radiation is similar to that expected from a sample containing a pre-determined amount of the tracer compound. It is not necessary to calculate the concentration of tracer compound in the target sample from the value of the measured property but it is within the scope of the invention to do so if convenient. The display may be visible to the vehicle driver by mounting the display on or near the dashboard of the vehicle. In addition or as an alternative the display may be located in a position where it is visible from outside the vehicle so that the condition of the urea in the tank of the vehicle may be easily determined by the vehicle operator or a regulatory officer. Alternatively the indication means may comprise an electrical signal sent to a receiver mounted on the vehicle. Such a receiver may be associated with a vehicle tachograph or other recording means. As a further alternative the indication means may transmit a signal to a remote receiver by means of a telecommunications or radio system such as SMS short messaging or an equivalent service for example. A geographical positioning system may be associated with the apparatus to provide information concerning the location of the apparatus when the analysis for tracer composition is made. The geographical information may be added to any transmitted or stored analysis result so that the location of the vehicle when the measurement is made can be recorded. This may be of use to identify the source of a urea solution which does not contain the correct concentration of the tracer compound or to determine the expected characteristics of an added tracer composition if there is regional or commercial variation. The data output from the system also preferably includes a vehicle identifier so that the analysis may be attributed to the vehicle into which the fluid was introduced.

The tracer composition optionally comprises one or more secondary tracer compound(s) in addition to fluorescent or absorbent tracer compound(s). The secondary tracer compound may be detectable using an on-vehicle measurement apparatus as described above, but optionally it is detectable using an ex-situ apparatus. In the event that the measured property of the first tracer compound(s) deviate from the property of standard concentration in the liquid by more than a pre-determined amount, a sample may be taken for analysis in a laboratory or by a portable apparatus which is located outside the vehicle from which the sample has been taken. The additional tracer compound may be analysed by any suitable method. It is not necessary for the additional tracer to be identified "in the field" since it is used to confirm the analysis of the first tracer in case a discrepancy from the expected result is found or tampering is suspected. Thus the additional tracer may be detectable using spectroscopic methodology, e.g. infra-red

chromatography, coupled with a suitable detector or by comparison with standard chromatograms.

In a specific embodiment of the system, the secondary tracer may comprise a phenol, i.e. phenol or a substituted phenol. Suitable substituted phenols include alkyl phenols e.g. 2-methyl phenol, 2-ethylphenol, alkoxy phenols e.g. 3-ethoxy phenol; hydroxy-phenols, e.g. catechols, hydroquinone. It is preferred that the phenol is not para-substituted with an alkyl, aryl, nitro, benzoyl, nitroso or aldehyde group. The concentration of the phenol in the aqueous liquid is preferably in the range from 0.1 – 20 ppm w/v. A phenol tracer is preferably measured using a spectrophotometric method involving the coupling reaction between the phenol and 4-aminoantipyrine in the presence of an initiating compound. Alternative methods may be used, such as the coupling of the phenol with 3-methyl-2-benzothiazole hydrazone, which is a known analytical method for the determination of phenol in water. The coupling of phenols with 4-aminoantipyrine to form a chromophore is a well-known analytical method to measure the amount of phenols in wastewater or for use in enzymatic methods for analysis of body fluids, e.g. the determination of cholesterol in blood. The method of such analysis is therefore well known to the skilled person. A description of such methods is found in Lupetti et al, Talanta 62 (2004) 463-467; ASTM D1783 Test method B; APHA Standard Method 5530D and EPA Methods for Chemical Analysis of Water and Wastes, Method 420.2.

The coupling of phenols with 4-aminoantipyrine (4-AAP) to form a chromophore takes place in alkaline solution in the presence of an initiator. The coupling reaction requires one mole of 4-AAP per mole of phenol. The 4-aminoantipyrine solution is normally aqueous and may contain from about 0.5 to about 30g per litre, more preferably from about 1 - 20 g per litre. The amount of 4-aminoantipyrine used should be sufficient to couple all of the phenol in the sample and is preferably present in sufficient amount to provide an excess of 4-AAP e.g. at least 1.5 moles of 4-AAP per mole of phenol, e.g. from about 2 to about 5 moles of 4-AAP per mole of phenol. Since the amount of phenol expected to be present in the sample is known (because the amount of tracer added to the aqueous liquid is known) it is possible to calculate the required amount and concentration of 4-AAP reagent to be used. The pH is preferably in the range from 9.8 to 10.2. The initiating compound is normally potassium ferricyanide, or where the presence of ammonia is likely, an alternative initiator such as a persulphate, especially sodium persulphate, may be used. The initiator is present at a concentration sufficient to initiate the coupling of the 4-aminoantipyrine with a phenol to form a chromophore. Normally from about 1 mole to at least 20 moles of initiator are provided per mole of 4-aminoantipyrine. The chromophore exhibits strong absorbance of light in the region 500 – 510 nm. The absorbance is proportional to the concentration of the chromophore in the solution, according to the Beer-Lambert law and the absorbance is therefore proportional to the concentration of phenol in the sample. Changes in

that exhibited by the aqueous liquid when the tracer compound had been added indicate that the liquid sample has been diluted or otherwise changed from its original composition. The absorbance of the solution may be measured using a conventional laboratory or a hand-held spectrophotometer.

When the tracer composition comprises more than one first tracer compound and/or additional secondary tracer compound(s), the ratio of each tracer compound to each other tracer compound in the tracer composition may be selected to be a unique identifier for each aqueous liquid or source of aqueous liquid to be tagged. Thus by selection of the nature and concentration of each tracer compound in a tracer composition, the aqueous liquid, when tagged may bear a unique "fingerprint" which may be used to identify product in a way which is difficult for a non-authorised person to replicate. One particular use for the combination of tracers is for the identification of particular batches of the aqueous liquid, e.g. for verification of the date of manufacture to ensure that the product is sold within the shelf-life of the aqueous liquid.

The tracer composition may optionally contain, in addition to the tracer compound (or more than one tracer compound), one or more other components such as a diluent, a solvent, a dye, a dispersant, or a surfactant. The identity and amount of the components of the tracer composition is normally confidential to the source producer of the product. The tracer composition is preferably a liquid but may also be provided in solid form if it is capable of being dissolved in the aqueous liquid without difficulty. If provided in solid form then additives may be present to enhance and facilitate the dissolution of the tracer composition in the aqueous liquid.

The system of the invention is particularly suitable for tagging and identifying genuine AdBlue AUS32 urea solution for use in heavy duty and lighter diesel engine SCR apparatus.

The method of the invention is further described with reference to the accompanying drawings in which:

Figure 1 is a diagram of a verification system according to the invention;

Figure 2A – 2C represent schematically an analytical apparatus suitable for use in the present invention;

Figure 3 is a plot of fluorescence emission against concentration of a urea solution in water for tracers A and B.

Fig 1 shows diagrammatically a verification system installed on a diesel engine-powered vehicle. The vehicle is fitted with a tank 10 for containing a urea solution. The tank includes a filling port 34 through which a solution of urea may be added to the tank, e.g. by pumping from a storage tank or simply by pouring from a portable container. The tank also includes a conduit 36 through

from the engine. The system comprises a switch 12 which is associated with a system control computer 16. The switch may be activated by the flow of fluid into the tank through the filling port. An analytical instrument 14 may be triggered by the control computer 16 to initiate an analysis by the activation of the switch 12. The analytical instrument is, in this particular embodiment, a fluorimeter comprising a probe having a source of excitation radiation arranged to irradiate a space within the probe, and a detector for detecting fluorescent radiation emitted from a liquid sample contained within the space. The probe is arranged with respect to the tank in such a way that the space within the probe which is irradiated is filled with a sample of fluid as the fluid is filled into the tank. The analytical instrument further comprises means to transfer information concerning the detected radiation from the detector to the control computer. The control computer 16 and a GPS apparatus 18 are housed within a protective housing 20 mounted within the vehicle. The housing 20 also contains a data output device 22 adapted to transmit data to a data storage means 24 and data transmission equipment 26, capable of transmitting data via a SMS "short messaging service" telecommunications system to a remote database 28 which is not mounted on the vehicle. The data output device is also capable of transmitting data to an on-board information system 30 located on the vehicle, such as a tachograph and/or a display visible to the driver or other person filling the tank. The system components also include at least one power supply 32, which may draw power from the vehicle power supply or from a dedicated battery. The power supply supplies power to all of the powered components of the system, i.e. the analytical equipment, switch, communications systems and control equipment.

The verification system also includes a tracer compound which is added to authentic supplies of the urea solution at a point in the supply chain before the urea solution is supplied for filling into a vehicle tank. The tracer compound is added to provide a pre-determined standard concentration of tracer in the urea solution. The tracer compound is a fluorescent compound having a characteristic excitation and emission energy. The tracer compound is soluble in the urea solution. The source of excitation radiation is selected to be of a wavelength which is close to the wavelength of maximum absorption of the tracer compound. The detector is adapted to detect radiation having a wavelength at or near the wavelength of maximum emission which is characteristic of the tracer compound. In this way, the analytical instrument is adapted to detect the presence of the selected tracer compound which is a part of the verification system of the invention and to measure the concentration of the tracer compound in the fluid which is analysed.

The operation of the system will now be explained. When a fluid is introduced into the tank through the filling port, the switch 12 is activated. The control computer 16 then sends a signal to the analytical instrument 14 to initiate the measurement of fluorescent radiation emitted from the fluid in the probe when it is irradiated by the radiation source. The measurement is sent by the detector to the control computer, where it may be stored and used to calculate a derived

concentration, calculated from a calibration stored within the control computer or it may be a comparison of the measured fluorescence with a stored value representing the fluorescence measured in a standard sample of urea solution which contains the pre-determined standard concentration of the tracer compound. The raw data, or the derived parameter, is then sent to a data output device for transmission to a vehicle diagnostics system, a vehicle data recorder such as a tachograph, and/or a remote database, via the SMS communications system. The data output device also receives data from the GPS system so that the location where the fluid was filled into the tank may be recorded and transmitted with the tracer concentration data.

An embodiment of an analytical apparatus used in the method and system of the invention is shown schematically in figs 2A – 2C. The apparatus comprises a housing portion 50A which is generally hollow and has an inner surface 54 which does not reflect light. A glass tube 51 passes through the housing and is in communication with the tubing 52 and 53 at each end respectively. The tubing forms a conduit suitable for the passage of urea solution from a tank to the analytical apparatus and to the SCR system. The connection between the glass tube and the urea conduits is sealed against leakage by suitable couplings. Referring to Fig 2B, the apparatus further comprises housing portion 50B which is adapted to be assembled to housing portion 50A to form a light-tight housing. Fig 2C shows a cross-section through line A—A of the apparatus when it has been assembled. Portion 50B includes a recess 55 into which the glass tube 51 may be located when the housing portions 50A and 50B are assembled together. A LED 56 is located within the housing and is adapted to shine light of a selected wavelength across the recess towards photodiode 57, and through glass tube 51 when the housing is assembled. A second photodiode 58 is located at approximately 90 degrees from the LED and photodiode 57. Photodiode 58 is adapted to receive light of a pre-determined narrow band of wavelengths which band is at or includes the wavelength of maximum fluorescent emission of a selected fluorescent tracer compound. A filter may be present to modify the light received by the photodiode(s) 57 and /or 58 . An electronic control system, data processor and internal connections therewith are located within the housing 50B but not shown in the drawings. The apparatus is powered using the vehicle power, via the vehicle battery. Power and electrical signals to and from the apparatus enter the housing at 59. The housing may contain appropriate power transformers to be compatible with the vehicle power supply. Indicator lights 60, 61 are mounted to be visible from the outside of the housing. Indicator light 60 is illuminated when the apparatus is receiving power. Indicator light 61 is preferably a triple-colour LED capable of shining red, green and yellow depending upon the signal received.

In use, the apparatus is mounted between the urea storage tank and the SCR system of a vehicle. Urea passes from the storage tank to the SCR system through the glass tube 51 and tubes 52 / 53. Light from the LED 56 passes through the glass tube into the urea solution and

detect the amount of light of the selected excitation wavelength that is transmitted through the solution and tube 51. This information may be processed by the data processor to determine a variety of conditions. Firstly a reduction in the amount of transmitted light can indicate that the tube 51 has become less transparent, e.g. due to the build up of deposits on the surface of the tube. A reduction in the light received by the reference detector 57 may also be caused by a faulty LED source. The brightness of the LED and thus the amount of excitation energy generated affects the amount of fluorescence generated by the solution. The data-processor is capable of calculating from the light received by the reference detector the amount of fluorescence which would be generated by a standard urea solution containing a pre-determined concentration of the tracer compound from the energy emitted by the source LED and therefore the measurement may by adjusted for the brightness of the LED. The transmitted light can also be used to obtain information about the concentration of the urea solution. A typical solution of urea at a concentration of about 32%w/v is slightly cloudy and may also appear slightly red. If the solution is significantly diluted then more light can pass through the solution so the photodiode 57 receives more light. The data processor is capable of comparing the light received by photodiode 57 with a standard data set generated by a standard solution. A deviation from the amount of light transmitted by a standard solution may indicate that a non-standard urea solution is in use in the vehicle and an appropriate warning condition may be generated. When no solution is present in the glass tube between the source and detector then the amount of light received by the photodiode may be significantly increased and such a condition may indicate the absence of solution between the LED source and the reference detector, which may be due to an airlock in the glass tube. When any warning or fault condition is detected, an appropriate signal is generated and indicator light 61 becomes yellow or red. In such a case a signal may also be sent to a warning system in the driver's cab or a remote monitoring station.

When the solution contains a fluorescent compound as a tracer, the fluorescent light emitted from the solution impinges upon photodiode 58, which is the fluorescence detector . The amount of light at the pre-determined band of wavelengths received by photodiode 58 is monitored by the data-processor. When the light received by the detector 58 is within a pre-determined amount (e.g. + / - 5%) of the calibrated amount for a standard tagged urea solution then the signal sent by the data-processor causes the indicator light 61 to glow green. If the amount of light monitored at the fluorescent emission wavelengths is different from the amount which would be emitted from a urea solution containing the standard level of tracer composition then the status of the solution may be registered as "non-standard". The status is shown by indicator light 61 which glows red, and is preferably also recorded in a data-store within or remote from the vehicle. Data concerning the amount of light transmitted by and / or emitted by a standard urea solution containing a particular pre-determined amount of a selected fluorescent tracer is generated by calibrating the apparatus in the known way and storing the calibration in the data processor.

In an Example of a verification system and method according to the invention, two fluorescent tracer compounds A and B were added to a 32.5% aqueous solution of urea, each at a concentration of 50 ppb w/v. The fluorescence of the solution was measured by irradiating with light from at 280nm a source fitted with a 10nm band-pass filter and the fluorescence monitored at 320 – 360nm and 400 – 460nm, which encompasses the wavelength of maximum fluorescent emission of the tracer compounds. The solution was then diluted successively to 90, 75, 50, 25% with water and the fluorescence was measured after each dilution. A further measurement was made using water instead of urea solution. The fluorescence of each solution is shown plotted in Fig 3 as counts at maximum emission for each tracer.

Claims

1. A system for the verification of an aqueous liquid comprising

a) a tracer composition comprising a first tracer compound, optionally at least one secondary tracer compound and optionally a solvent, the tracer composition being soluble in said aqueous liquid

b) analytical apparatus adapted to measure a property of a target sample of said liquid, which property varies according to the concentration of said first tracer compound in the solution, and compare said measured property with the same property measured for a standard sample of the liquid containing a pre-determined amount of said first tracer compound

said analytical apparatus being mounted on or within said vehicle, and

c) an indicating means for indicating when the difference between the property measured for the target sample of the liquid and the property of the standard sample of the liquid exceeds a pre-determined value.

2. A verification system according to claim 1, wherein the analytical apparatus comprises one or more of: an emission spectrometer, an ion mobility spectrometer, a mass spectrometer, an absorption spectrometer, a surface acoustic waveform detector and an amplifying fluorescent polymeric sensor.

3. A verification system according to claim 1 or claim 2, wherein the tracer composition comprises one or more of: a fluorescent compound, a radiation absorbing compound, an alcohol, an organic acid and a carbohydrate.

4. A verification system according to any of claims 1 - 3, comprising:

(i) a tracer composition comprising at least one tracer compound capable of absorbing radiation of a wavelength in the range 200 – 1100nm,

and

(ii) a portable analytical apparatus mounted on or within a vehicle, comprising

f) a source of excitation radiation, adapted to irradiate a target sample of the aqueous liquid with light at a predetermined wavelength, said predetermined wavelength being selected to be capable of being absorbed by at least one of said tracer compounds,

g) a radiation detector arranged to detect radiation emitted from or transmitted by the sample,

h) a data collection and manipulation device for gathering data from the radiation detector and producing information concerning the intensity and wavelength of the emitted or transmitted radiation detected by the radiation detector,

i) data-processing means for comparing the characteristics of intensity and wavelength of

radiation source with the characteristics of radiation emitted from or transmitted by a standard sample containing a predetermined concentration of the tracer compound, and

j) indication means to indicate whether the characteristics of the light emitted from or transmitted by the target sample are within a predetermined range of the characteristics of the light emitted from or transmitted by the standard sample.

5. A system as claimed in claim 3 or claim 4, wherein the tracer compound is a fluorescent compound.

6. A system as claimed in any one of the preceding claims, wherein the tracer compound is present in the liquid at a concentration in the range from 1 ppb - 20 ppm w/v.

7. A system as claimed in claim 5 or claim 6, wherein the fluorescent compound is excited by radiation of a wavelength in the range from 250 – 700 nm and emits fluorescent radiation at a wavelength in the range from 300 – 800 nm.

8. A system as claimed in any one of the preceding claims, wherein said analytical apparatus is located within said vehicle and adapted to measure the concentration of tracer compound in a target sample of the liquid within a container for the liquid or within a conduit communicating with said container.

9. A system as claimed in any one of the preceding claims, further comprising a switch and a control apparatus arranged such that the switch, upon actuation by a stimulus, sends a signal to said control apparatus and said control apparatus, upon receipt of the signal, initiates an analytical procedure carried out by the analytical apparatus.

10. A system as claimed in any one of the preceding claims, further comprising a data storage device.

11. A system as claimed in any one of the preceding claims, further comprising a geographical positioning apparatus associated with said data processor and/or a data storage device such that the location of the vehicle at the time of the measurement of the concentration of said tracer compound may be recorded.

12. A system as claimed in any one of the preceding claims, further comprising transmitter for transmitting data generated by said data –processing means to a remote receiver associated with a data storage facility.

13. A system as claimed in any one of the preceding claims, wherein said indication means comprises a signal which is visible to an operator of the vehicle.

14. A system as claimed in any one of the preceding claims, wherein the aqueous liquid comprises a urea solution suitable for use in a process for the selective catalytic reduction of nitrogen oxides emitted from a diesel engine mounted in a vehicle, said aqueous urea solution comprising from 30 – 35% of urea.

15. A method of characterising a urea solution used in a selective catalytic reduction process for treating emissions from the engine of a vehicle, by comparison with a reference standard sample of a urea solution containing a pre-determined amount of a tracer compound, comprising analysing a target sample of said urea solution to measure a characteristic property of said tracer compound in said sample and comparing the measured property with the property measured by analysing said reference standard sample of a urea solution, characterised in that the analysis of the urea solution and the comparison of the measured characteristic property of the target sample of urea solution with that of the reference standard sample is performed using analytical apparatus mounted on or within said vehicle.

16. A method as claimed in claim 15, wherein said apparatus comprises an indicating means for indicating when the difference between the concentration of said first tracer in the target sample of the urea solution and the concentration of tracer in the standard sample of the urea solution exceeds a pre-determined value.

17. A method according to claim 15 or 16, wherein the analysis of the target sample of urea solution is carried out before the sample of urea solution enters a urea storage vessel located on or in the vehicle.

18. A method according to claim 15 or 16, wherein the target sample of urea solution has been withdrawn from a urea storage vessel located on or in the vehicle.

19. A method according to claim 15 or 16, wherein the analysis of the target sample of urea solution is carried out using an analytical apparatus comprising a probe located within a urea storage vessel located on or in the vehicle.

20. A method as claimed in any one of claims 15 - 19, wherein said analytical apparatus comprises

a) a source of radiation, adapted to irradiate said target sample of urea solution with light at a predetermined wavelength, said predetermined wavelength being selected to be

b) a radiation detector arranged to detect radiation emitted from or transmitted by the target sample,

c) a data collection and manipulation device for gathering data from the radiation detector and producing information concerning the intensity and wavelength of the emitted or transmitted radiation detected by the radiation detector and data-processing means for comparing the characteristics of intensity and wavelength of the light emitted from or transmitted by the target sample when irradiated by said radiation source with the characteristics of radiation emitted from a standard sample of the liquid containing a known quantity of the tracer compound, and

d) indication means to indicate whether the characteristics of the light emitted from or transmitted by the target sample are within a predetermined range of the characteristics of the light emitted from or transmitted by the standard sample.

21. An analytical apparatus comprising

e) a source of radiation, adapted to irradiate a target sample of an aqueous liquid with light at a predetermined wavelength, said predetermined wavelength being selected to be capable of being absorbed by at least one of said tracer compounds,

f) a radiation detector arranged to detect radiation emitted from or transmitted by the target sample,

g) a data collection and manipulation device for gathering data from the radiation detector and producing information concerning the intensity and wavelength of the emitted or transmitted radiation detected by the radiation detector and data-processing means for comparing the characteristics of intensity and wavelength of the light emitted from or transmitted by the target sample when sample is irradiated by said radiation source with the characteristics of radiation emitted from a standard sample of the liquid containing a known quantity of the tracer compound, and

h) indication means to indicate whether the characteristics of the light emitted from or transmitted by the target sample are within a predetermined range of the characteristics of the light emitted from or transmitted by the standard sample

characterised in that the radiation source and detector are mounted on or within a vehicle and are adapted to irradiate and detect radiation emitted from or transmitted by a sample of a urea solution used in a selective catalytic reduction process for treating emissions from the engine of a vehicle.

22. An apparatus as claimed in claim 21, wherein the radiation source and detector are adapted to irradiate and detect radiation emitted from or transmitted by a sample of a urea solution located within a urea solution container mounted on or in the vehicle or within a conduit communicating with said container.

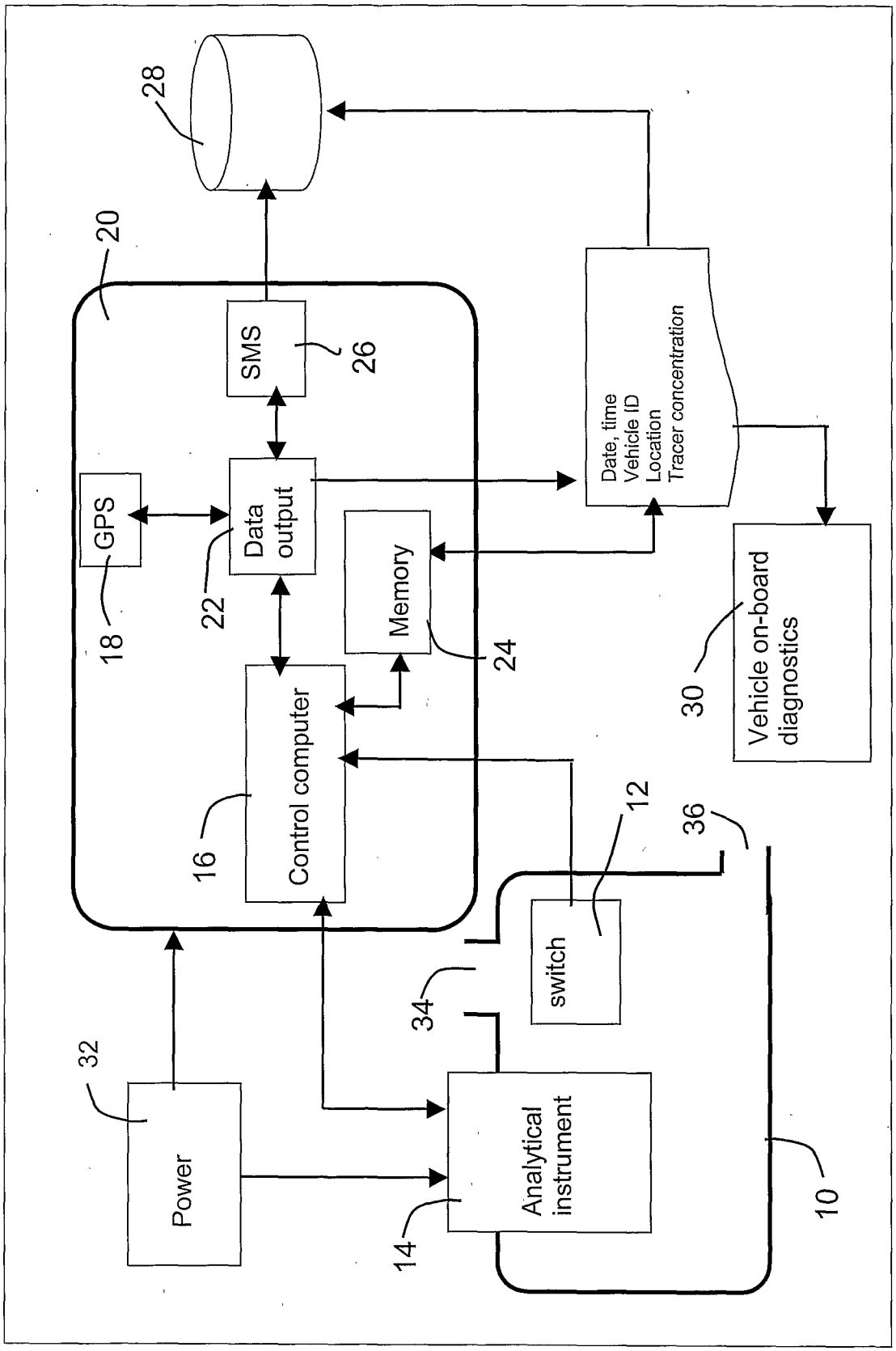
23. An apparatus as claimed in claim 21 or 22, wherein the radiation source and detector are located within said urea solution container or within a conduit communicating with said container.

24. An apparatus as claimed in claim 21 or 22, wherein the radiation source and detector are located outside said urea solution container or conduit communicating with said container.

25. A vehicle having a diesel engine, a selective catalytic reduction apparatus for treating gaseous emissions from said engine, and a container for containing an aqueous urea solution for use in the selective catalytic reduction apparatus, characterised in that said vehicle further comprises an analytical apparatus adapted to measure a characteristic property of a tracer compound contained in said urea solution, the analytical apparatus being located to analyse a target sample of the aqueous urea solution within said container or within a conduit associated with said container.

26. A vehicle according to claim 25, wherein said analytical apparatus comprises one or more of: an emission spectrometer, an ion mobility spectrometer, a mass spectrometer, an absorption spectrometer, a surface acoustic waveform detector and an amplifying fluorescent polymeric sensor.

27. A vehicle according to claim 25, wherein said analytical apparatus comprises an analytical apparatus according to any one of claims 21 - 24.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SMS
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Date, time
Vehicle ID
Location
Tracer concentration
GPS
18
Data output
22
Memory
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Vehicle on-board diagnostics
30
Control computer
16
12
36
switch
34
32
Power
Analytical instrument
14
10

Figure 1

Figure 2A

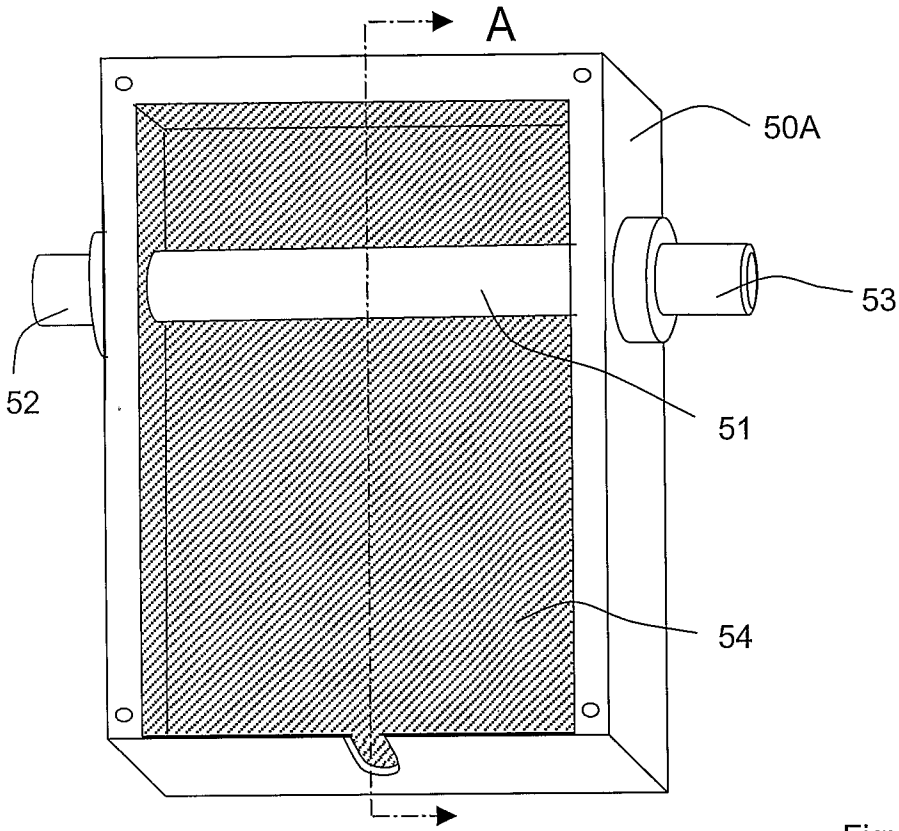


Figure 2B

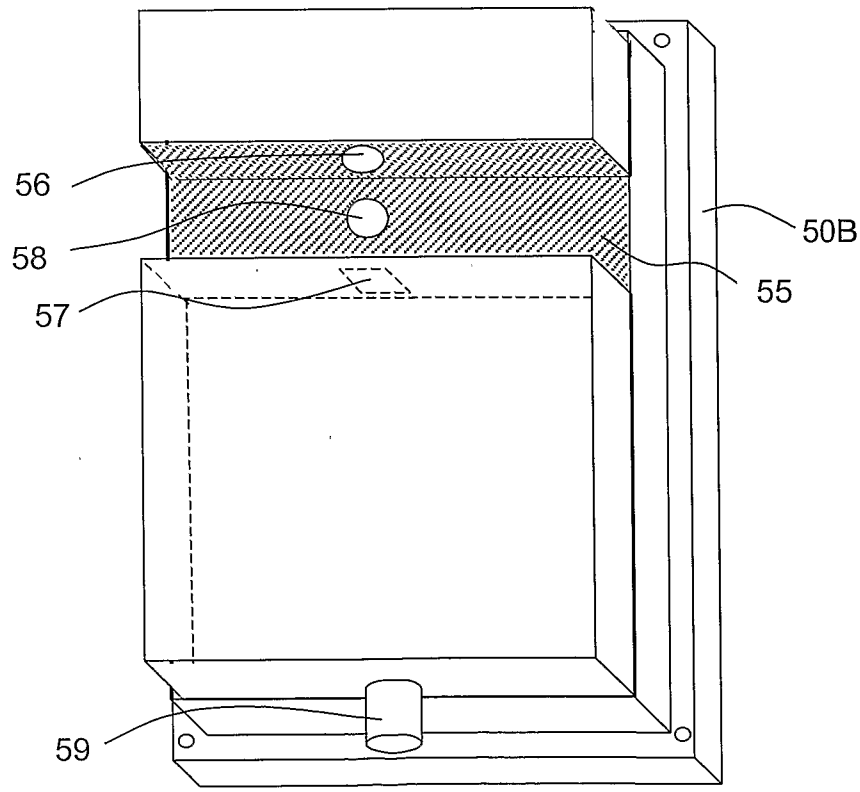


Figure 2C

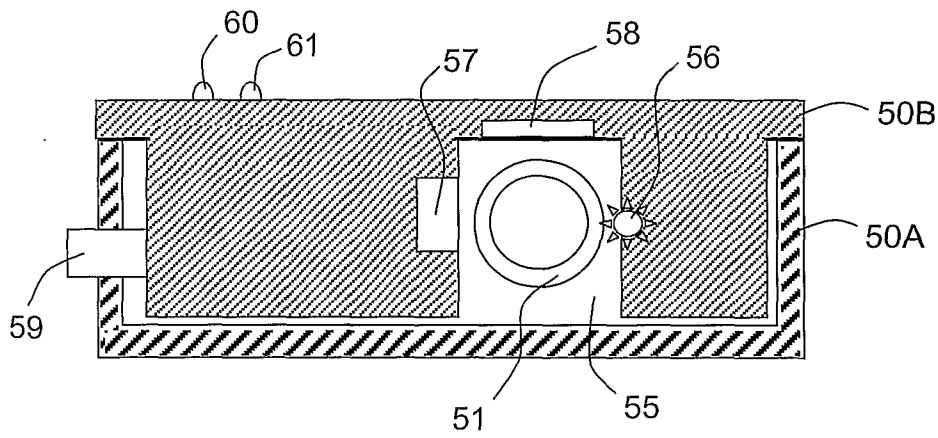
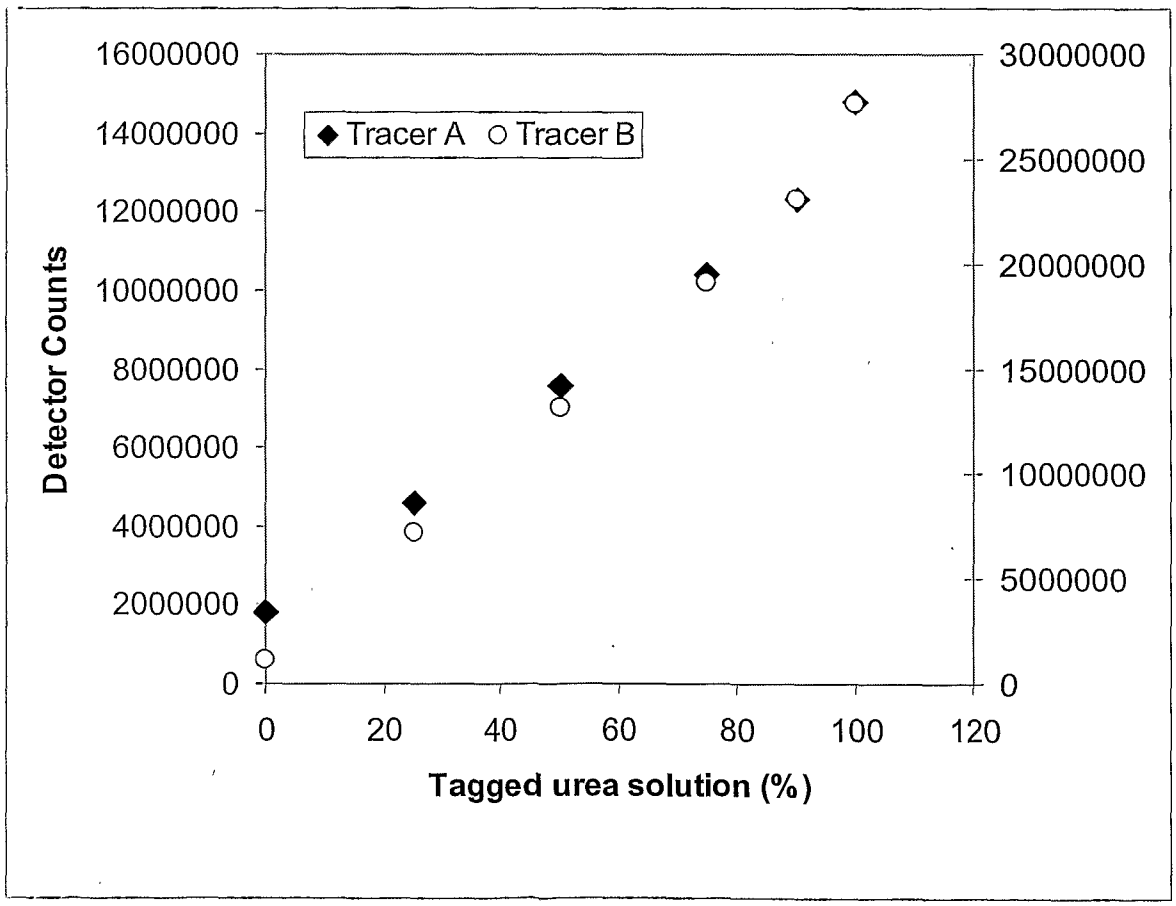


Figure 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2007/001626

A. CLASSIFICATION OF SUBJECT MATTER
INV. F01N3/20 C01C1/08 G01N33/50

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)
F01N C01C

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 practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/75643 A1 (CLEAN DIESEL TECH INC [US]; BANKS RODNEY HOWARD [US]; DUBIN LEONARD [U) 14 December 2000 (2000-12-14) page 8, line 6 - page 9, line 6; figures page 13, line 27 - page 14, line 12	1-10, 12-27
A	US 2005/207936 A1 (BERRYHILL ROSS C [US] ET AL) 22 September 2005 (2005-09-22) the whole document	1-27
A	US 5 132 096 A (HOOTS JOHN E [US] ET AL) 21 July 1992 (1992-07-21) the whole document	1-27
A	US 5 277 135 A (DUBIN LEONARD [US] ET AL) 11 January 1994 (1994-01-11) the whole document	1-27

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 August 2007	23/08/2007

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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