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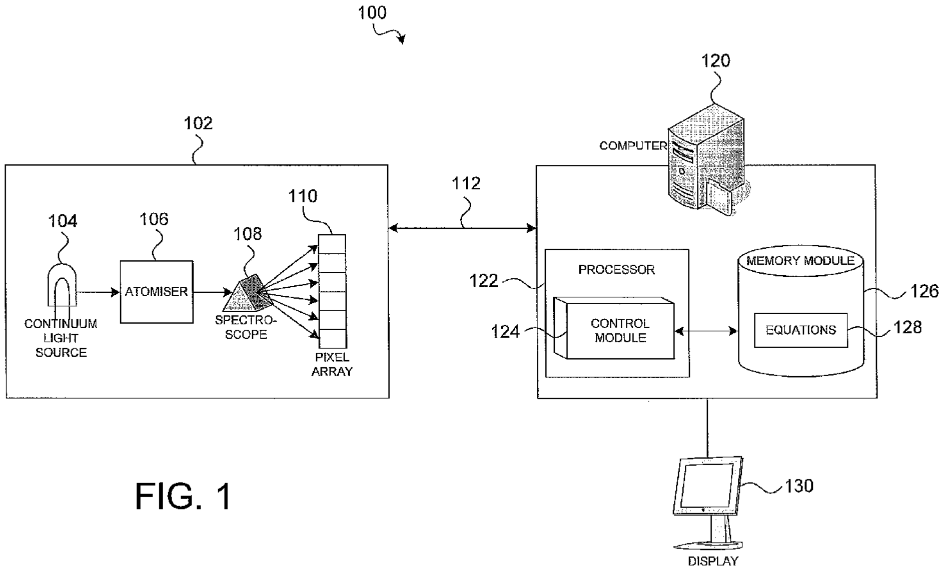

FIG. 1

(57) Abstract: This invention relates to an atomic absorption spectrometer (AAS) (102) to an AAS system (100) and to a method (200) of atomic absorption spectrometry. The AAS (102) includes an electromagnetic (BM) radiation emitter (104) operable to emit a radiation continuum across a broad spectrum and a detector arrangement including a spectrograph (108) and an array of photo-sensitive pixels (1 10), the spectrograph (108) being operable to spread EM radiation across the entire broad spectrum at once to the array of pixels (1 10) to measure radiation across the entire broad spectrum. The AAS (102) further includes an electro-thermal atomiser (106) operable to vaporise an analyte to a high vapour density and a control module (124) operable to calculate and linearise the function of absorbance against concentration of the analyte vapour in the atomiser (106) based on the measured radiation.

Atomic absorption spectrometry

FIELD OF INVENTION

THIS INVENTION relates generally to atomic absorption spectrometry and particularly to an atomic absorption spectrometer and a method of atomic absorption spectrometry.

BACKGROUND

The Inventor is aware that, in atomic absorption spectrometry (or spectroscopy), electromagnetic radiation is directed at a sample, the composition of which is to be analysed. The presence and concentration of a particular element is determined based on an amount of radiation absorbed by the sample vapour at a particular wavelength. Each element has a characteristic absorption wavelength (or combination of wavelengths) which uniquely differentiates it from other elements.

In traditional Electrothermal Atomic Absorption Spectrometry (ETAAS), electromagnetic radiation (e.g. light) from a linear spectrum light source passes through the cavity of a fast heated graphite tube atomiser [1]. The sample is fully vaporised in an argon atmosphere from the wall or special substrate (platform) in the centre of the tube. The cavity serves as absorption volume, and the sample vapour is transported from the centre to the open ends of the tube on account of diffusion or argon flow. Radiation corresponding to specific resonance line λ_l in the spectrum of the element to be determined (analyte) is monitored as electric output of the detector, $I_0(\lambda_l)$ and $I_t(\lambda_l)$, before and during the vaporisation pulse, respectively. Time dependent linear absorbance $A_t(\lambda_l) = \log[I_0(\lambda_l)/I_t(\lambda_l)]$ is used to characterise an amount of atomic vapour of the analyte N_t in the vapour phase. At low absorbance ($A_t(\lambda_l) < 0.3 \div 0.4$ for the most sensitive atomic lines) N_t is proportional to A_t; above that limit function $A_t(\lambda_l)$ vs. N_t depends on a structure of the spectral line and characteristics of the radiation source. Total amount of the analyte in the sample N_0 within the proportionality range $A_t(\lambda_l)$ vs. N_t is thus characterised by the absorption peak area:

$$N_0 \approx (\tau)^{-1} \cdot \int_0^{\infty} A_t(\lambda_l)dt\,, \qquad (1)$$

where τ is residence time of atoms in the absorption volume. Calibration of the measurements is performed using the reference material with known content N_0 (parameter τ is considered to be equal for the analyte from the sample and reference material).

The use of integration (1) under conditions of full atomisation provides independence of the determination results from the analyte release rate out of the sample and reference material. Since atomic absorption can be accompanied by non-specific attenuation of light due to presence of matrix, various instrumental methods are used in analytical practice to separate atomic absorption from the background (BG correction) [1]. Limit of detection (LOD) for a particular element is determined mainly by sensitivity of the absorption line, ability of the atomiser to create high pulse density of atomic vapour and level of fluctuations, $\delta I_0(\lambda_l)$ and $\delta I_t(\lambda_l)$ at low absorption. The error caused by fluctuations of radiation from the light source is normally reduced using special optical arrangements (e.g. a double-beam arrangement). Effect of random fluctuations on LOD depends on intensity of radiation and broadening of line profile in the light source. The measurements for specific analyte and respective calibration are performed using similar experimental conditions. Each measurement includes the sampling and run of temperature program specific for the analyte and major sample components, which normally includes drying, thermal pre-treatment, atomization and cleaning steps that altogether takes time about 1 minute or more. Dilution of the sample between sequential measurements is needed to provide absorbance within the linearity range $A_t(\lambda_l)$ vs. N_t. The measurements for various analytes are performed sequentially with the use of specific light sources matched to each analyte.

Within the last 10-15 years, the status of ETAAS as the most popular technique for determination of trace elements has been reduced owing to fast development and broad distribution of ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) and ICP-MS (Inductively Coupled Plasma Mass Spectrometry) instrumentation for multi-element analysis. The main reason for the decrease of interest in ETAAS is its slowness due to the necessity of exchange of spectral lamps and sample dilution according to the content of each analyte and sensitivity of respective lines. Nevertheless, ETAAS still remains cost effective and, in general, less prone to interferences when compared to other methods of analytical atomic spectrometry. Advancement of ETAAS into the range of multi-element methods would provide new analytical opportunities such as drastic reduction of the determination time and determination of elements ratio in each single sample. The most successful attempts to make multi-element instrument based on traditional AAS approach were realised by combination of four light sources and respective similar optical arrangements with a single ET atomiser (e.g. Perkin Elmer SIMAA 6000 spectrometer [2]).

The alternatives to traditional ETAAS have been discussed comprehensively by Harnly [3] and Welz et al [4]. They associate prospects of multi-element determination by ETAAS with the use of high resolution (HR) spectral instrumentation, continuum light source (CS) and charge coupled device (CCD) detection with fast repetitive scanning of specific narrow spectral area. Currently, this concept is used for sequential determination of elements in a graphite tube atomiser with fast readjustment of analytical lines (contrAA® 700 HR-CS AA spectrometer, Analytic Jena [5]). In each measurement the spectral area 0.5 nm width including the analytical line is selected using high resolution double echelle monochromator. This area, containing 500 CCD pixels (with a wavelength increment of about 0.0018 nm per pixel), is scanned using frequency $1{\cdot}10^{-2}$ s^{-1} (10 ms per scan) sufficient for processing a 1-3 s vaporisation pulse typical for a graphite tube ETAAS.

In the HR-CS AA spectrometer, a concentration of analyte atoms in the absorption volume is measured using absorption at wavelength λ within the absorption profile, $A_t(\lambda) \cong A(p_\lambda, n)$, where p and n are pixel and scan numbers respectively, and p_λ is the pixel between p_{+w} and p_{-w} adjacent the absorption line. High resolution provides the width of instrumental profile close to that of the absorption line that guarantees proportionality $A(p_\lambda, n)$ vs. N_t within the range $A(p_\lambda n) < 1$ [4]. This permits the use of absorption maximum corresponding to pixel $p_{\lambda m}$,

$$N_t \propto A(p_{\lambda m}, n), \tag{2}$$

or linear combination

$$N_t \propto A(p_{\lambda m}, n) - A(p_{\lambda m \pm w}, n), \tag{3}$$

where $A(p_{\lambda m \pm w}, n)$ is average of $A(p_{\lambda m+w}, n)$ and $A(p_{\lambda m-w}, n)$, for characterisation of atomic vapour content in the absorption volume, N_t. Equation (3) permits correction of the non-specific spectral background next to the absorption line, $A(p_{\lambda m \pm w}, n)$ and use of the sum of all scans for characterisation of full amount of the analyte in the sample,

$$N_0 \propto \sum_n [A(p_{\lambda m}, n) - A(p_{\lambda m \pm w}, n)]. \tag{4}$$

If the scanning frequency is sufficient, the summation (4) becomes equal to temporal integration

$$\theta \sum_n [A(p_{\lambda m}, n) - A(p_{\lambda m \pm w}, n)] \cong \int_0^\infty A_t(\lambda_m) dt, \tag{5}$$

where θ is time between sequential scans that provides independence from the vaporisation rate of the analyte.

A high resolution instrument provides effective separation of analytical lines of different elements that guaranties low probability of spectral interferences. On the other hand, the lines of several elements can be detected with an HR instrument and used for true simultaneous determination only if they belong to the selected narrow spectral area (0.5 nm for the instrument described in [4]), which can be scanned fast to provide large enough number of scans during the vaporisation pulse. However, the number of lines which meet this requirement is limited; the determination sensitivity with these lines is normally much lower than that for the analytical lines situated beyond the scanned interval [6]. These factors prevent the use of an HR CS ETAAS instrument for true simultaneous multi-element determination. Although the analysis time is much shorter compared with traditional AAS methodology due to the presence of only one light source, the determination of various elements has to be performed sequentially using repetitive sampling.

In order to provide true simultaneous ETAAS determination of several elements from a single sample with a continuum light source, a spectral range between 200 and 400 nm is needed where the main sensitive resonance lines normally used in AAS, are situated. In this spectral area the number of CCD pixels should be large enough to resolve main absorption lines of various metals. On the other hand, the pulse character of atomic absorption signals necessitates a high speed of data collection that limits a number of CCD pixels to be used for the measurements. This trade-off presents a difficulty in using electrothermal atomisation in HR CS AAS for simultaneous multi-element determination. Another difficulty relates to providing broad determination ranges for various elements without dilution of the sample.

The Inventor believes that it is not practicable to provide high spectral resolution (i.e. small individual wavelength increments between the neighbouring pixels) as well as a broad spectrum. For example, if the above array of pixels were to be extended to cover a broad spectrum from 200 nm to 400 nm (for a range of 200 nm) having a high resolution (with a wavelength increment of about 0.0018 nm per pixel), the array would need about 110000 pixels. Fast data collection from such number of pixels is impossible or impracticable using present day techniques. Similar problems should also persist if a high resolution spectrum is presented in a broad wavelength area as several strings of lines (in echelle spectrograph), and two-dimensional CCD is used for the data collection [3].

The inventor wishes to overcome or at least alleviate the sequential sampling drawback of AASs.

SUMMARY OF INVENTION

According to one aspect of the invention, there is provided an atomic absorption spectrometer (AAS) which includes:

an electromagnetic (EM) radiation emitter operable to emit a radiation continuum across a broad spectrum;

a detector arrangement including a spectrograph and an array of photo-sensitive pixels, the spectrograph being operable to spread EM radiation across substantially the entire broad spectrum at once to the array of pixels to measure radiation across substantially the entire broad spectrum;

an electro-thermal atomiser operable to vaporise an analyte; and

a control module operable to calculate and linearise the function of absorbance against concentration of the analyte vapour in the atomiser based on the measured radiation.

In the context of this specification, “broad spectrum” refers to a spectral range (e.g. 200 nm) which includes absorption wavelengths of a plurality of elements, while "narrow spectrum" refers to a spectral range (e.g. 1nm) centred at or near the absorption line of a specific element, with a small tolerance either side. The broad spectrum may be at least one, and optionally two or more, order of magnitude wider than the narrow spectrum.

The AAS may be a low or high resolution AAS. It is to be appreciated that the pixel array of a low resolution, wide spectrum AAS in accordance with the invention may have a similar number of pixels as that of a high resolution, narrow spectrum AAS in accordance with the prior art. Thus, the pixel array itself may be similar to those of prior art AASs. The pixel array (of the AAS in accordance with the invention) may, for example, include between 3000 and 4000 pixels.

The EM radiation emitter may include a single continuum light source, which may, for example, have a broad emission spectrum of at least 200 nm to 400 nm.

The spectrograph may be configured to spread substantially the entire broad spectrum across the pixel array in relatively large increments per pixel. Therefore, in the case of a broad spectrum of 200 nm to 400 nm and a pixel array having 4000 pixels, the wavelength increment may be approximately 0.05 nm.

The AAS may include a housing which defines therein an absorption volume and which accommodates, in use, a vapour sample to be analysed. The AAS may then measure the concentration of one or more elements comprising the vapour sample.

The AAS may include an electronic processor. The control module may be a conceptual module which corresponds to a functional task performed by the processor. The AAS may include a machine-readable medium, main memory, and/or a hard disk drive, which carries a set of instructions to direct the operation of the processor, the set of instructions for example being in the form of a computer program.

The control module (or other controller operatively connected to the array of pixels) may be operable to take a measurement from the array of pixels at a plurality of periodic time intervals, e.g. 4 ms, for a pre-defined or pre-definable period, e.g. 1 s to 3 s.

It is to be understood that the processor may be one or more microprocessors, controllers, digital signal processors (DSPs), or any other suitable computing device, resource, hardware, software, or embedded logic. It is also to be understood that the control module need not necessarily be consolidated into the same device as the EM radiation emitter and the detector arrangement. For example, the control module may be hosted by a remote computer which is connectable to the device housing the EM radiation emitter and the detector arrangement.

Accordingly, the invention extends to an AAS system which includes:

an AAS device which includes

an electromagnetic (EM) radiation emitter operable to emit a radiation continuum across a broad spectrum;

a detector arrangement including a spectrograph and an array of photo-sensitive pixels, the spectrograph being operable to spread EM radiation across substantially the entire broad spectrum at once to the array of pixels to measure radiation across substantially the entire broad spectrum; and

an electro-thermal atomiser operable to vaporise an analyte; and

a computer in communication with the AAS device, the computer being operable to receive from the AAS device a communication indicative of measured radiation and including a control module operable to calculate and linearise absorbance based on the measured radiation.

The control module (whether part of the AAS defined above or part of the AAS system defined above) may be operable to calculate absorbance from the radiation measured by respective pixels. More particularly, the control module may be operable to square respective calculated absorbances and to sum the squared absorbances (see equation (11) below) to provide an indication of concentration of an analyte within a sample in the atomiser.

The control module may be configured to apply at least one of the equations (or mathematical equivalents thereof) selected from the group composed of equations (10) to (17) defined below.

The definition and description of the invention assumes a high degree of atomisation and similar residence time of atoms evolved from the sample and reference material in the absorption volume.

The array of pixels may be a provided by one selected from the group comprising a Charge Coupled Device (CCD) array (or at least be connected to a CCD arrangement) and a Diode Array Detector. Contemporary linear CCD array may consist of about 4000 pixels, which can be scanned into memory of the computer every 4 ms [7]. This frequency is sufficient for detecting an atomisation pulse.

If the continuum light source provides high enough light output, and the CCD array of pixels (in accordance with the invention) may detect the entire spectrum in the 200 nm to 400 nm range, the wavelength increment would be 0.05 nm per pixel, that is more than 25 times higher than that in HR CS AAS described above (in accordance with the prior art).

According to another aspect of the invention, there is provided a method of atomic absorption spectrometry, the method including:

directing an EM radiation emitter at a vapour sample to be analysed, the emitter being operable to emit EM radiation across a broad spectrum;

spreading substantially the entire broad spectrum at once across an array of pixels,

measuring radiation received by the array of pixels across substantially the entire broad spectrum; and

calculating and linearising absorbance based on the measured radiation.

The method may include pulse-vaporisation and atomisation of the sample.

The method may include summing a plurality of sequential linearised absorbances to determine, or at least provide an indication, of the amount of an element in a sample.

The calculation and linearising of the absorbance and summation of the linearised absorbance may be done automatically and electronically, for example by a control module as defined above. At least some of the method steps may be repeated periodically at intervals (e.g. 10 ms) for a duration of an atomisation pulse (e.g. 1 s to 3 s). The method may include a prior step of analysing a reference sample.

The calculation, linearising and summing may be done in accordance with at least one of the equations (or mathematical equivalents thereof) selected from the group composed of equations (10) to (17) defined below.

The invention extends to a machine-readable medium having stored thereon a set of instructions which, when executed by a machine, causes the machine to perform a method as above defined.

Without wishing to be bound by theory, the Inventor puts forward the following. Reduction of the resolution of a spectral instrument causes broadening of the absorption line. The resulting wavelength distribution $A'_t(\lambda)$ is determined by convolution of the line profile $A_t(\lambda)$ at given experimental conditions and instrumental transmittance profile $F(\lambda)$,

$$A'_t(\lambda) = \int_{-\infty}^{\infty} F(\lambda')A_t(\lambda - \lambda')d\lambda'. \qquad (6)$$

If the line half width is small in comparison with the half width of the instrumental profile (that is correct for low resolution instruments normally used in atomic spectrometry), then

$$A'_t(\lambda) \propto F(\lambda) \cdot \int_{-\infty}^{\infty} A_t(\lambda')d\lambda' = F(\lambda) \cdot S_t, \qquad (7)$$

where

$$S_t = \int_{\lambda} A_t(\lambda)d\lambda, \qquad (8)$$

comes from properties of the convolution [8]. Therefore, at any point of the resulting profile, absorbance should be proportional to the wavelength integrated absorbance S_t. The absorbance maximum should be reduced, compared to that for HR instrument, approximately proportional to the respective resolution ratio, depending on the half width of the instrumental transmittance profile $F(\lambda)$. Accordingly, a higher amount of the analyte should be introduced in the atomiser of the low resolution instrument to obtain measurable signals.

High vapour density, in turn, creates additional obstacle for the element determination with a continuum light source, indicated in the theory and experiment [3, 9]. The vaporisation of large amounts of the analyte is accompanied by change of function S_t vs. N_t: above some absorption level, the alteration from $S_t \propto N_t$ to $S_t \propto \sqrt{N_t}$ occurs. The inflection point of the respective functions depends on individual characteristics of the atomic line; the combined function $S_t = f(N_t)$ cannot be quantitatively predicted [3]. This uncertainty does not allow using of temporal integration $A'_t(\lambda)$ (according to equation (1)) for quantification of the absorption measurements.

If it is assumed that a high density of atomic vapour in the atomiser is provided, e.g. on account of large sample mass or instant sample vaporisation, then only part of the combined function, which is $S_t \propto \sqrt{N_t}$, remains significant. This assumption makes basis for the following statement: if high density of atomic vapour in the absorption volume is provided, then equation

$$N_t \propto [A'_t(\lambda)]^2 \qquad (9)$$

should be correct for the absorption lines of the analyte.

For the low resolution AAS with CCD detection, linearisation (9) can be automatically introduced into the absorbance data for each pixel p_λ. Then, the pixel corresponding to absorption maximum, $p_{\lambda m}$, or any linear combination of pixels within the broadened by instrument line profile, can be used for characterisation of atomic vapour content in the absorption volume.

The linearisation (9), however, should not be applied directly for low signals overlapped by short noise, since it would transform all negative oscillations around the baseline into positive causing accumulation of integration error. To avoid this complication, the modification of equation (9),

$$N_t = a_p \cdot [A'(p_\lambda, n)]^2 \cdot sign[A'(p_\lambda, n)] \qquad (10)$$

is suggested, where *sign* is a function equal to +1 or -1, if $A'(p_\lambda, n)$ > or < 0, respectively, and a_p is a sensitivity coefficient for the particular pixel. For the signals above the noise level, (10) is equal to (9). Otherwise, short noise causes random deviations similar to that in the traditional or HR-CS ETAAS.

In the absence of non-specific spectral background, the amount of a particular element N_{0e} in the sample can be found using linearisation (10) and summation of absorbance data at absorption maximum (at the pixel $p_{\lambda m}$),

$$N_{0e} = a_e(p_{\lambda m}) \cdot \frac{\theta}{\tau_e} \cdot \sum_n \{[A_e'(p_{\lambda m}, n)]^2 \cdot sign[A_e'(p_{\lambda m}, n)]\} \qquad (11)$$

where τ_e is residence time of atoms of a particular element in the absorption volume. Thus, the $A_e'(p_{\lambda m}, n)$ data obtained during sample vaporisation, and the set of respective coefficients $a_e(p_{\lambda m}) \cdot \frac{\theta}{\tau_e}$ determined by calibration, should permit simultaneous determination of several elements.

If atomic spectrum is overlapped by non-specific attenuation of light, the output of the pixels at the centre of atomic line, $I(p_{\lambda m}, n)$, should be corrected to discard the non-specific constituent. This can be performed under the suggestion that the fine structure of the molecular bands, possibly overlapping atomic absorption line, is not resolved and other sources of background produce an absorption continuum. Under those conditions, BG correction can be performed using the admission that average output $I(p_{\lambda m \pm \Delta}, n)$ of pixels $p_{\lambda m+\Delta}$ and $p_{\lambda m-\Delta}$ on the distance Δ from $p_{\lambda m}$ within the line profile is equal to $I_0(p_{\lambda m}, n)$. Thus, BG corrected absorbance

$$\overline{A}_e(p_{\lambda m}, n) = \log[I_e(p_{\lambda m \pm \Delta}, n) / I_e(p_{\lambda m}, n)] \qquad (12)$$

can be used in the linearisation and temporal summation, similar to (10) and (11),

$$N_{te} \propto [\bar{A}_e(p_{\lambda m},n)]^2 \cdot sign\bar{A}_e(p_{\lambda m},n) \tag{13}$$

and

$$N_{0e} = a_e(p_{\lambda m}) \cdot \frac{\theta}{\tau_e} \cdot \sum_n \{[\bar{A}_e(p_{\lambda m},n)]^2 \cdot sign[\bar{A}_e(p_{\lambda m},n)]\} \tag{14}$$

If, in some possible cases, the overlapping of the absorption lines of different elements cannot be neglected, a correction algorithm based on linearity of function (9) for any pixel within the absorption line profile should be introduced. For example, in a case of two overlapping line profiles, belonging to elements $e1$ and $e2$ with maximums at pixels $p_{\lambda m1}$ and $p_{\lambda m2}$, respective contents of the elements N_{01} and N_{02} can be presented via system of linear equations

$$[(a_{e1}(p_{\lambda m1}) \cdot \frac{\theta}{\tau_{e1}})]^{-1} \cdot N_{01} + [(a_{e2}(p_{\lambda m1}) \cdot \frac{\theta}{\tau_{e2}})]^{-1} \cdot N_{02} = \sum_n [\bar{A}(p_{\lambda m1},n)]^2 \cdot sign[\bar{A}(p_{\lambda m1},n)] \tag{15}$$

$$[(a_{e1}(p_{\lambda m2}) \cdot \frac{\theta}{\tau_{e1}})]^{-1} \cdot N_{01} + [(a_{e2}(p_{\lambda m2}) \cdot \frac{\theta}{\tau_{e2}})]^{-1} \cdot N_{02} = \sum_n [\bar{A}(p_{\lambda m2},n)]^2 \cdot sign[\bar{A}(p_{\lambda m2},n)] \tag{16}$$

Similar systems of q equations for q elements and q pixels can be solved numerically using, e.g. matrix inversion method [10]. The solution matrix is to be obtained by multiplication the matrix ***C*** of summations $\sum_n [\bar{A}(p_{\lambda mq},n)]^2 \cdot sign[\bar{A}(p_{\lambda mq},n)]$ for each pixel from $p_{\lambda m1}$ to $p_{\lambda mq}$ by the inverse matrix ***A*** of coefficients $\frac{a_{eq}(p_{\lambda m1 \div q})}{\tau_{eq}}$, determined independently for each element from e_1 to e_q,

$$\boldsymbol{X}=\boldsymbol{A}^{-1}\cdot\boldsymbol{C}. \tag{17}$$

An AAS in accordance with the invention provides true simultaneous multi-element determination using a low resolution CCD spectrometer, which broadens the absorption lines more than 10-20 times compared to natural line width at the ET vaporisation experimental conditions.

The determination of several elements may be performed using the information obtained during sample vaporisation within a single run of temperature programme and calibration data obtained independently.

BRIEF DESCRIPTION OF DRAWINGS

The invention will now be further described, by way of example, with reference to the accompanying diagrammatic drawings.

In the Drawings,

Figure 1 shows a schematic view of an AAS system in accordance with the invention;

Figure 2 shows a flowchart of a method in accordance with the invention;

Figures 3 and 4 show, respectively, the measured CCD output and peak atomic absorption for the sampled solution 10 ppm Ag and 5 ppm Na and Mg in water;

Figure 5 shows absorption spectrum corresponding to Figure 3 after linearisation of the measurements according to equation (10);

Figure 6 shows profile of absorption line Ag 328.068 before and after linearisation of the measurements (a and b, respectively);

Figure 7 shows Ag atomic absorption pulse before and after linearisation (a and b, respectively);

Figure 8 shows integrated absorbance for 64 ppb (parts per billion) Mn and the highlighted pixels used for background correction according to equations (12) and (14), where Δ=2;

Figures 9A and 9B show Mn (64 ppb) atomic absorption at Mn 279.482 nm spectral line calculated according to equations (12) and (14) without (A) and with (B) correction to short noise;

Figure 10 shows spectrum of integrated linearised absorbances for the solution 8 ppm (part per million) Ag, Bi, Cd, Ga, In, Mn, Mg, Na, K, Pb and Tl; and

Figures 11 and 12 show the determination ranges for Cd, Ga, In, Tl and Ag, Bi, Mn, Pb, respectively, in the mixed solutions of equal amounts of Ag, Bi, Cd, Ga, In, Mn, Mg, Na, K, Pb, and Tl.

DETAILED DESCRIPTION OF EXAMPLE

Referring to Figure 1, reference numeral 100 generally indicates an AAS system in accordance with the invention. The AAS system 100 comprises an AAS device 102 and a computer 120 operatively connected to the AAS device 102 via a communication link 112.

The AAS device 102 has a light source 104 which is operable to emit EM radiation having a continuum spectrum in a range, for example, 200 nm to 400 nm. The radiation is directed at an absorption cavity of an atomiser 106. The atomiser 106 includes a graphite furnace (not illustrated) to vaporise a sample. Once the radiation has passed through the absorption cavity, it is directed to a spectrometer 108 which spreads the entire broad spectrum at once across an array of pixels 110. The array of CCD pixels 110 communicates information indicative of measured radiation across the communication link 112 to the computer 120.

The computer 120 has a processor 122 and a memory module 126. The processor 122 has a control module 124 which is operable to calculate and linearise absorption based on radiation measurements using the array of pixels 110 in accordance with equations 128 stored on the memory module 126. The equations 128 for example are equations (10) to (17) defined above. The computer 120 further has a display 130 which is operable to provide an indication to a user of the system 100 of the elements determined by the control module 124 to be present in the sample as indicated by equations 128.

Referring now to Figure 2, a high-level flow diagram illustrates a method of atomic absorption spectrometry indicated by reference numeral

200. The method 200 includes directing, at block 202, EM radiation having continuous broad spectrum at a sample to be analysed. Once the radiation has passed through the sample vapour, the entire radiation is spread, at block 204, at once across an array of pixels. The radiation received by the array of pixels is measured, at block 206, across the entire broad spectrum and the amount of radiation measured by each pixel is processed, at block 208, for example using equations (10) to (17) defined above, to calculate absorbance which is then linearised and summed.

The elemental composition of the sample is then displayed, at block 210. If desired, a reference sample can be analysed, at block 201, for calibration purposes.

The method 200 may conveniently be implemented on the system 100, although its application is not necessarily limited to such a system.

EXPERIMENT

Instrumentation and procedure

The experiments were performed using an Ocean Optics HR4000 spectrometer (the abbreviation HR in the sense of "high resolution" is used by the manufacturer as a trademark for a specific type of Ocean Optics instruments; it should not be confused with the corresponding term employed in this specification) equipped with a grating 1200 grooves per mm and 5 µm spectral slit; and coupled with a xenon arc lamp (L 2479, 300 W, Hamamatsu, Japan) and a fast heated ballast furnace atomiser [11]. The spectra within 190 nm to 410 nm wavelength area were registered using Toshiba 3680 pixels CCD and a PC (analogous to the computer 120 of Figure 1). The design of the atomiser and respective power supply provided a heating rate of the furnace 10 K/ms and temperature stabilisation at the pre-set level; the ballast delayed the vaporization of the analyte thus providing vapour enter in the absorption volume at high temperature. Optimal sampling volume for the fast heated ballast atomiser was 10 µL.

The measurements included two runs of temperature program (refer to Table 1) with and without sampling the sample solution, spectra acquisition during the atomisation step, and sequential transfer of the CCD outputs with and without sample ($I(p,n)$ and $I_0(p,n)$, respectively) to Microsoft Excel worksheets. The number of spectra collected during the atomisation step that is 80, was limited by Excel software. Maximal size of each $I(p,n)$, $I_0(p,n)$ Excel worksheet was 3680×80 cells; of that number 18×80 cells were used for automatic correction of dark current.

In the first set of experiments, the evolution of atomic absorption spectra of 10 ppm Ag, Bi, Cd, Ga, In, Mg, Mn, Na, K, Pb and Tl were registered during the vaporisation of individual analytes, the suggested calculation algorithm investigated and calibration matrix ***A*** (see equation 17) composed. In the second set, absorption spectra from the mixed solutions of the same elements were detected, determination range and limit of detection for each element in the mixture determined. Volatile elements were chosen for the experiments to avoid possible “memory” effects after sampling high concentrations of the analytes. However, to eliminate “memory”, additional cleaning of the atomiser from the remnants of samples was performed by 3 to 4 runs of temperature programme between the measurements. Relatively rare elements Ag, Bi, Cd, Ga, In, Mn, Pb and Tl were chosen in order to avoid non-controllable contamination of the solutions. Mg, Na and K were added to the list as most characteristic components of environmental samples.

Spectral distribution of electric output from the CCD pixels during one of the scans within the atomisation cycle of Ag is shown in Figure 3: two absorption lines, Ag 328.068 and 338.289 [4] appear simultaneously with absorption at Mg and Na lines caused by contaminations. The data obtained from both blank, $I_0(p,n)$, and sample, $I(p,n)$, measurements were used for absorbance calculation, $A'(p,n) = LOG(I_0(p,n)/I(p,n))$. The absorption spectrum corresponding to the radiation spectrum, Figure 3, is shown in Figure 4. All above mentioned atomic lines are present in the absorption. Intense short noise in the short wavelength area is caused by low radiation output of the Xe lamp and sensitivity of the CCD detector in this wavelength region.

The spectrum reported in Figure 4, after linearisation of the measurements according to equation (9), is shown in Figure 5 as “linearised absorbance”. Squaring of the absorbance for each pixel resulted in substantial reduction of signal to noise ratio (Figure 5), reduction of half width of the absorption lines and absorption pulses, as it is shown in Figures 6 and 7, for Ag.

It was confirmed that the use of blank measurements for absorption calculation could cause an integration error because of relatively slow deviations of radiation flux from the lamp. This issue is illustrated by Figure 8 where three Mn absorption lines are present in the temporary integrated spectrum together with absorption continuum. Apparently, in practise, similar background can be caused by overlapping of atomic spectrum and molecular absorption continuum from specific matrices. The error can be eliminated or at least reduced by using equations (12) and (14), for background correction, where Δ depends on specific line. In the example, Figure 8, for the line Mn 279.482 nm parameter Δ is selected equal to 2 and the pixels equidistant from the central one are highlighted).

Reduction of concentration of the analytes in the sampled solution is accompanied by increase of contribution of short noise in the integrated linearised absorbance for any element to be determined. For small signals, the linearisation of measurements by simple squaring, according to equation (10), becomes improper: all statistical deviations of signal around zero line after squaring become positive (Figure 9A). The use of function SIGN, in equations (13) and (14), eliminates the error and restores statistical character of noise.

The spectrum of integrated linearised absorbance for the mixed samples calculated according to equation (14) includes 1 to 3 of the most sensitive resonance line of each element (Figure 10). Variation of mixed sample composition from 200 ppm to 2.5 ppb of Ag, Bi, Cd, Ga, In, Mn, Pb and Tl outlines the determination range for each metal with the lines in Figure 10. The respective calibration curves appeared to be linear within 4.5 to 5 orders of magnitude (Figures 11 and 12). The limitation at low concentrations, most probably, relates to the residual “memory” effect that can be further reduced by optimisation of the atomiser and temperature program.

The linearity of calibration curves (Figures 11 and 12) permitted the evaluation of determination sensitivity using the data for individual elements, and calculation of limits of detection (LOD). Respective data for the lines in Figure 10 are presented in Table 2, where the units $(\text{absorbance})^2 \times \text{s/ng}$ are employed for sensitivity characterisation. To avoid overestimation LOD, the ballast furnace with residual “memory” (already exposed to more than 400 runs of a temperature programme with various concentrations of analyte) was employed; blank measurements were repeated 10 times. For each analytical line, standard deviation (STDEV) of integrated linearised absorption was calculated, and the value 3 (STDEV) normalised to the sensitivity data was taken as LOD. The data on LOD for flame atomic absorption from “Varian guide to ICP/AAS analytical values” [12] are reported in Table 2 for comparison. The comparison shows that, in general, simultaneous ETAAS provides limits of detection similar to those of sequential flame AAS. LOD for Cd and Pb, for simultaneous ETAAS, are poorer than in flame AAS because of low radiation from the lamp in short wavelength area (Figure 3).

Although all main analytical lines in the diagram, Figure 10, are resolved, possible superposition of less sensitive lines should not be ignored. To provide necessary correction, the reference data matrix ***A*** (see equations 15 to 17) is to be composed from the measurement data for each single element. According to the requirements of matrix inversion method [10], only one line of each element could be presented in the reference matrix. The example of matrix composed for the constituents of the tested mixture is presented in Table 3. The diagonal members of the matrix characterise the determination sensitivity at most sensitive for each particular element wavelengths (Table 2, column 3).

The information regarding atomic absorption of each element in the sample compiled data matrix ***C*** in Table3; the solution of 2.5 ppm Ag, Mn, Pb and Tl was employed as a test sample. The multiplication of the inversed matrix ***A*** by matrix ***C*** gives the resulting matrix ***X***. In the example (Table 3) the determination results for all four metals are very close to the known concentrations that points out to the absence or efficient correction of spectral interferences.

Conclusion

The example shows that the invention provides the methodology of fast simultaneous determination of plurality of elements within broad concentration range and limits of detection close to those in traditional flame atomic absorption spectrometry with sequential determination of elements.

The concentration range can be still enlarged and limits of detection reduced an account of radiation source, more efficient in the short wavelength area (e.g. similar to that used in HR CS AAS [4]) and increase of data collection frequency using special software. The determination errors caused by residual memory can be reduced by optimisation of temperature program and gas flow during the cleaning step.

The most probable application, as it is seen from the determination range, is in the field where a flame AAS is still extensively used. Apart of dramatic reduction of determination time, the analytical advantages characteristic for ET AAS, e.g., related to matrix modification, thermal pre-treatment of the sample and temporal separation of interfering spectra should also attract attention to the invention. The substitution of flame to electrothermal atomisation should also permit getting rid of specific safety problems connected with storage and use of flammable gases and open the way to miniaturisation of the AAS instrumentation.

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[12] http://www.varian.com

TABLES

Table 1. Temperature program used for simultaneous ET AAS determination in the fast heated ballast furnace

Step	Temperature, ºC	Ramp time, s	Hold time, s	Gas*, L/min
drying	100	5	15	0.5
Pyrolysis 1	500	5	15	0.5
Pyrolysis 2	500	1	1	0
Vaporization	2400	0	2	0
Cleaning	2600	1	2	0.5

* Argon flow near the ends of the furnace

Table 2. Determination sensitivity and limits of detection for simultaneous ET AAS.

Element	Line, nm	Sensitivity (A^2s)/ng	3 STDEV* A^2s	LOD, ng	LOD**, µg/L	LOD***, µg/L
Ag	328.068	0.45	0.037	0.082	8.2	2
Ag	338.289	0.26	0.023	0.089	9	
Bi	306.772	0.074	0.013	0.175	17.5	50
Cd	228.802	1.32	0.174	0.132	13.2	2
Ga	294.364	1.0	0.026	0.026	2.6	100
Ga	287.424	0.45	0.005	0.011	1.1	
Ga	403.299	0.25	0.004	0.016	1.6	
In	303.936	0.64	0.029	0.045	4.5	40
In	325.609	0.33	0.007	0.021	2	
In	410.176	0.47	0.057	0.12	12	
Mn	279.482	0.96	0.054	0.056	5.6	2
Pb	283.306	0.16	0.027	0.173	17	
Pb	217.001	0.19	0.14	0.616	61.6	10
Tl	377.572	0.56	0.029	0.052	5.2	
Tl	276.787	0.59	0.039	0.066	6.6	16
Tl	237.958	0.18	0.03	0.162	16.2	

* - Standard deviation measured for 10 blank runs of temperature program, Table 1 in the furnace exposed to more than 400 measurements.
** - 10 µl sampling
*** - the data for sequential determination in flame AAS [12]

Table 3. Simultaneous determination of 2.5 ppm Ag, Mn, Pb and Tl in the mixed solution of 11 metals using reference data matrix (equation 17)

Reference data matrix, ***A***

Element, line, nm	Sensitivity, $(A^2s/ppm)\times10$										
	Ag	Bi	Cd	Ga	In	K	Na	Mg	Mn	Pb	Tl
Ag328.068	45.35622	0.069184	-0.00081	0.04799	-0.00322	-0.06851	-0.0425	-0.00114	0.00068	-0.0515	-0.03215
Bi306.772	0.001145	7.486943	-0.0003	0.07149	-0.00141	0.065058	0.043288	-0.00114	-0.00154	-0.00212	0.000712
Cd228.802	0.009092	0.031277	132.3436	0.061411	0.272953	0.340028	0.17778	0.098161	-0.02165	0.067188	0.000295
Ga294.364	-0.00404	-0.00284	0.0407	96.07707	0.14507	0.11867	0.102514	0.041141	0.00885	0.005181	-0.01304
In303.936	0.004422	-0.00169	0.085871	-0.00117	64.89891	0.163758	0.210051	0.093896	-0.00216	-0.00188	0.005146
K404.414	0.156206	0.21702	0.230047	0.20664	0.331197	14.35186	0.291527	0.229261	0.138829	0.176712	0.175578
Na330.237	6.067578	6.25125	5.988792	6.354333	6.43753	6.514576	56.63007	5.924741	5.921652	6.309352	6.442664
Mg285.213	18.43346	18.4124	20.04392	20.08409	18.53923	18.55039	35.66285	277.0629	17.21442	18.35184	18.25357
Mn279.482	0.072411	-0.14916	-0.09756	0.121726	0.035647	0.308509	0.179462	-0.01257	96.141	-0.27423	-0.17363
Pb283.306	0.003842	0.001605	0.000987	0.003227	0.006373	0.000208	-0.00811	0.012132	-0.0107	18.63851	0.000961
Tl377.572	0.00378	0.038736	-0.00992	0.010836	0.008539	-0.00335	0.011269	-0.00218	-0.00196	0.004273	60.64235

Element, line, nm	Sample data matrix, ***C*** A^2s	Results matrix, ***X*** ppm
Ag328.068	10.81714	2.38976
Bi306.772	0.015691	0.02021
Cd228.802	0.639332	0. 04688
Ga294.364	0.069699	0. 00713
In303.936	0.01593	0. 00182
K404.414	0.408565	0. 17015
Na330.237	6.228748	0. 0311
Mg285.213	19.05967	0. 01835
Mn279.482	24.76593	2.5856
Pb283.306	4.619684	2.47939
Tl377.572	15.91921	2.62487

$$\boldsymbol{X}=\boldsymbol{A}^{-1}\times\boldsymbol{C}$$

CLAIMS

1. An atomic absorption spectrometer (AAS) which includes:

an electromagnetic (EM) radiation emitter operable to emit a radiation continuum across a broad spectrum;

a detector arrangement including a spectrograph and an array of photo-sensitive pixels, the spectrograph being operable to spread EM radiation across the entire broad spectrum at once to the array of pixels to measure radiation across the entire broad spectrum;

an electro-thermal atomiser operable to vaporise an analyte; and

a control module operable to calculate and linearise the function of absorbance against concentration of the analyte vapour in the atomiser based on the measured radiation.

2. An AAS as claimed in claim 1, which is a low resolution, wide spectrum AAS.

3. An AAS as claimed in claim 1 or claim 2, in which the pixel array includes between 2000 and 4000 pixels.

4. An AAS as claimed in any of the preceding claims, in which the EM radiation emitter includes a single continuum light source.

5. An AAS as claimed in claim 4, in which the single continuum light source has a broad emission spectrum of at least 200 nm to 400 nm.

6. An AAS as claimed in any of the preceding claims, in which the spectrograph is configured to spread the entire broad spectrum across the pixel array in relatively large increments per pixel.

7. An AAS as claimed in any of the preceding claims, which includes a processor and in which the control module is a conceptual module which corresponds to a functional task performed by the processor.

8. An AAS as claimed in claim 7, which includes a machine-readable medium which carries a set of instructions to direct the operation of the processor.

9. An AAS as claimed in any of the preceding claims, in which the control module is operable to take a measurement from the array of pixels at a plurality of periodic time intervals for a pre-defined or pre-definable period.

10. An AAS system which includes:

an AAS device which includes

an electromagnetic (EM) radiation emitter operable to emit a radiation continuum across a broad spectrum;

a detector arrangement including a spectrograph and an array of photo-sensitive pixels, the spectrograph being operable to spread EM radiation across the entire broad spectrum at once to the array of pixels to measure radiation across the entire broad spectrum; and

an electro-thermal atomiser operable to vaporise an analyte; and

a computer in communication with the AAS device, the computer being operable to receive from the AAS device a communication indicative of measured radiation and including a control module operable to calculate and linearise absorbance based on the measured radiation.

11. An AAS system as claimed in claim 10, in which the control module is operable to calculate absorbance from the radiation measured by respective pixels.

12. An AAS system as claimed in claim 11, in which the control module is operable to square respective calculated absorbances and to sum the squared absorbances to provide an indication of concentration of an analyte within a sample in the atomiser.

13. An AAS system as claimed in any of claims 10 to 12 inclusive, in which the control module is configured to apply at least one of the equations (or mathematical equivalents thereof) selected from the group composed of:

$N_t = a_p \cdot [A'(p_\lambda, n)]^2 \cdot sign[A'(p_\lambda, n)]$;

$$N_{0e} = a_e(p_{\lambda m}) \cdot \frac{\theta}{\tau_e} \cdot \sum_n \{[A_e'(p_{\lambda m},n)]^2 \cdot sign[A_e'(p_{\lambda m},n)]\};$$

$$\overline{A}_e(p_{\lambda m},n) = \log[I_e(p_{\lambda m \pm \Delta},n) / I_e(p_{\lambda m},n)];$$

$$N_{te} \propto [\overline{A}_e(p_{\lambda m},n)]^2 \cdot sign\overline{A}_e(p_{\lambda m},n);$$

$$N_{0e} = a_e(p_{\lambda m}) \cdot \frac{\theta}{\tau_e} \cdot \sum_n \{[\overline{A}_e(p_{\lambda m},n)]^2 \cdot sign[\overline{A}_e(p_{\lambda m},n)]\};$$

$$[(a_{e1}(p_{\lambda m1}) \cdot \frac{\theta}{\tau_{e1}})]^{-1} \cdot N_{01} + [(a_{e2}(p_{\lambda m1}) \cdot \frac{\theta}{\tau_{e2}})]^{-1} \cdot N_{02} = \sum_n [\overline{A}(p_{\lambda m1},n)]^2 \cdot sign[\overline{A}(p_{\lambda m1},n)];$$

$$[(a_{e1}(p_{\lambda m2}) \cdot \frac{\theta}{\tau_{e1}})]^{-1} \cdot N_{01} + [(a_{e2}(p_{\lambda m2}) \cdot \frac{\theta}{\tau_{e2}})]^{-1} \cdot N_{02} = \sum_n [\overline{A}(p_{\lambda m2},n)]^2 \cdot sign[\overline{A}(p_{\lambda m2},n)];$$ and

$\boldsymbol{X} = \boldsymbol{A}^{-1} \cdot \boldsymbol{C}$.

14. An AAS system as claimed in any of claims 10 to 13 inclusive, in which the array of pixels is provided by one selected from the group comprising a Charge Coupled Device (CCD) array and a Diode Array Detector.

15. A method of atomic absorption spectrometry, the method including:

directing an EM radiation emitter at a vapour sample to be analysed, the emitter being operable to emit EM radiation across a broad spectrum;

spreading the entire broad spectrum at once across an array of pixels,

measuring radiation received by the array of pixels across the entire broad spectrum; and

calculating and linearising absorbance based on the measured radiation.

16. A method as claimed in claim 15, which includes pulse-vaporisation and atomisation of the sample.

17. A method as claimed in claim 15 or claim 16, which includes summing a plurality of sequential linearised absorbances to determine, or at least provide an indication, of the amount of an element in a sample.

18. A method as claimed in claim 17, in which the calculation and linearising of the absorbance and summation of the linearised absorbance is done automatically and electronically.

19. A method as claimed in any of claims 15 to 18 inclusive, in which at least some of the steps are repeated periodically at intervals for a duration of an atomisation pulse.

20. A method as claimed in any of claims 15 to 19 inclusive, which includes a prior step of analysing a reference sample.

21. A method as claimed in any of claims 15 to 19 inclusive, in which the calculation, linearising and summing is done in accordance with at least one of the equations (or mathematical equivalents thereof) selected from the group composed of:

$$N_t = a_p \cdot [A'(p_\lambda, n)]^2 \cdot sign[A'(p_\lambda, n)];$$

$$N_{0e} = a_e(p_{\lambda m}) \cdot \frac{\theta}{\tau_e} \cdot \sum_n \{[A_e'(p_{\lambda m}, n)]^2 \cdot sign[A_e'(p_{\lambda m}, n)]\};$$

$$\overline{A}_e(p_{\lambda m}, n) = \log[I_e(p_{\lambda m \pm \Delta}, n) / I_e(p_{\lambda m}, n)];$$

$$N_{te} \propto [\overline{A}_e(p_{\lambda m}, n)]^2 \cdot sign \overline{A}_e(p_{\lambda m}, n);$$

$$N_{0e} = a_e(p_{\lambda m}) \cdot \frac{\theta}{\tau_e} \cdot \sum_n \{[\overline{A}_e(p_{\lambda m}, n)]^2 \cdot sign[\overline{A}_e(p_{\lambda m}, n)]\};$$

$$[(a_{e1}(p_{\lambda m1}) \cdot \frac{\theta}{\tau_{e1}})]^{-1} \cdot N_{01} + [(a_{e2}(p_{\lambda m1}) \cdot \frac{\theta}{\tau_{e2}})]^{-1} \cdot N_{02} = \sum_n [\overline{A}(p_{\lambda m1}, n)]^2 \cdot sign[\overline{A}(p_{\lambda m1}, n)];$$

$$[(a_{e1}(p_{\lambda m2}) \cdot \frac{\theta}{\tau_{e1}})]^{-1} \cdot N_{01} + [(a_{e2}(p_{\lambda m2}) \cdot \frac{\theta}{\tau_{e2}})]^{-1} \cdot N_{02} = \sum_n [\overline{A}(p_{\lambda m2}, n)]^2 \cdot sign[\overline{A}(p_{\lambda m2}, n)]; \text{ and}$$

$$\boldsymbol{X} = \boldsymbol{A}^{-1} \cdot \boldsymbol{C}.$$

22. A machine-readable medium having stored thereon a set of instructions which, when executed by a machine, causes the machine to perform a method as claimed in any of claims 15 to 21 inclusive.

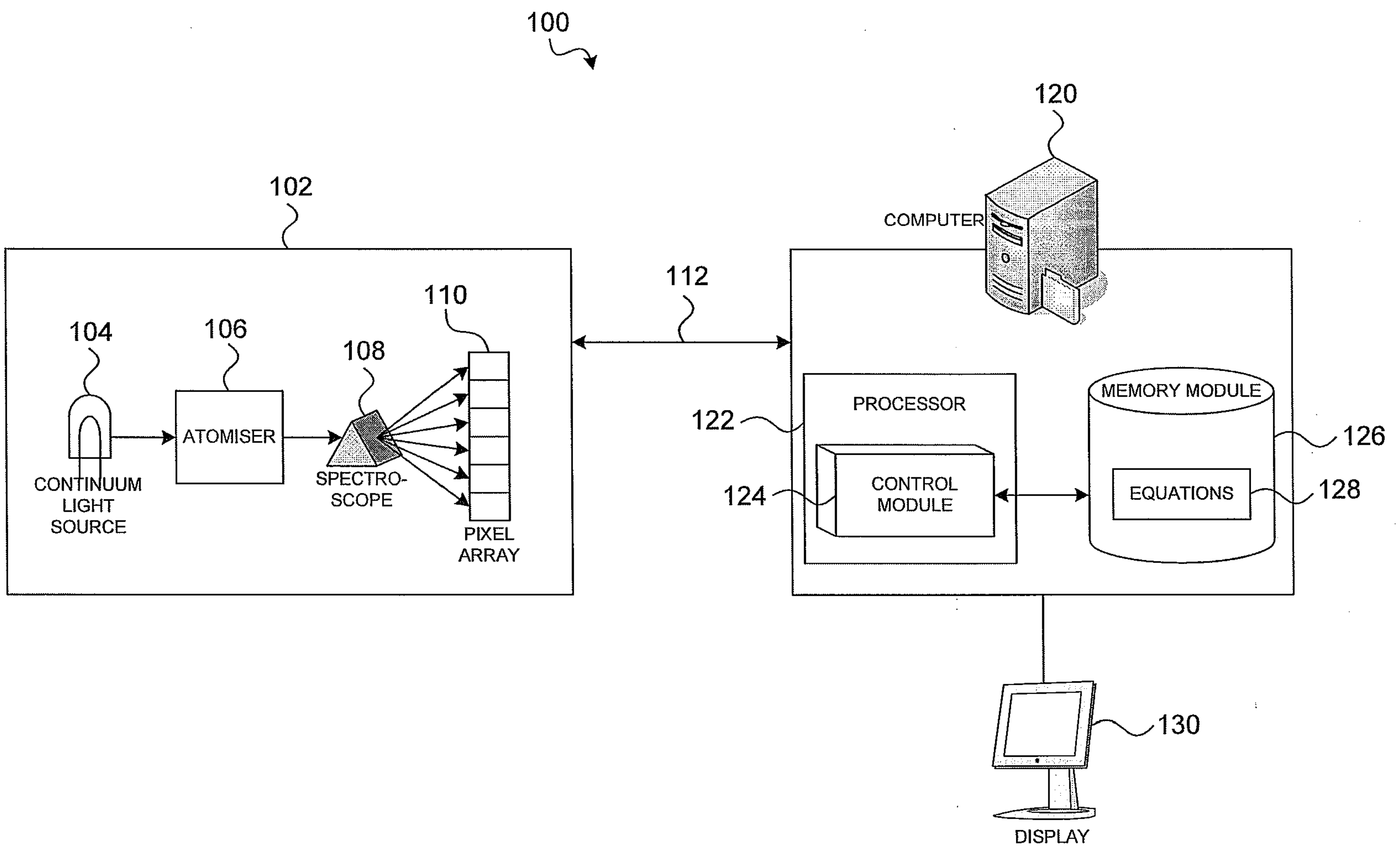
100
120
COMPUTER
102
112
104
106
108
110
CONTINUUM
LIGHT
SOURCE
ATOMISER
SPECTRO-
SCOPE
PIXEL
ARRAY
PROCESSOR
122
CONTROL
MODULE
124
MEMORY MODULE
126
EQUATIONS
128
130
DISPLAY

FIG. 1

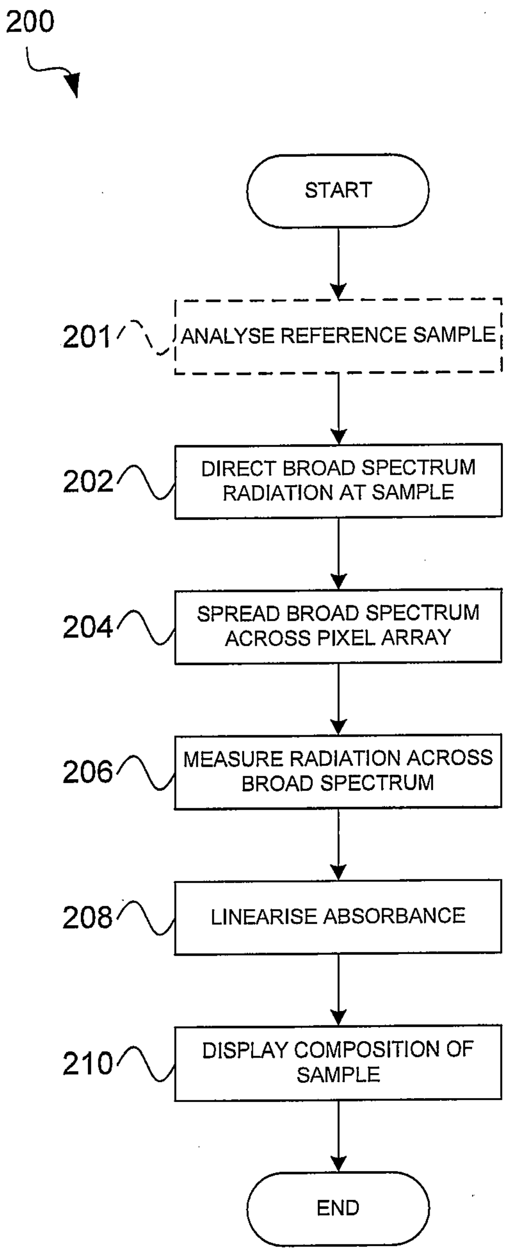
200
START
201
ANALYSE REFERENCE SAMPLE
202
DIRECT BROAD SPECTRUM RADIATION AT SAMPLE
204
SPREAD BROAD SPECTRUM ACROSS PIXEL ARRAY
206
MEASURE RADIATION ACROSS BROAD SPECTRUM
208
LINEARISE ABSORBANCE
210
DISPLAY COMPOSITION OF SAMPLE
END

FIG. 2

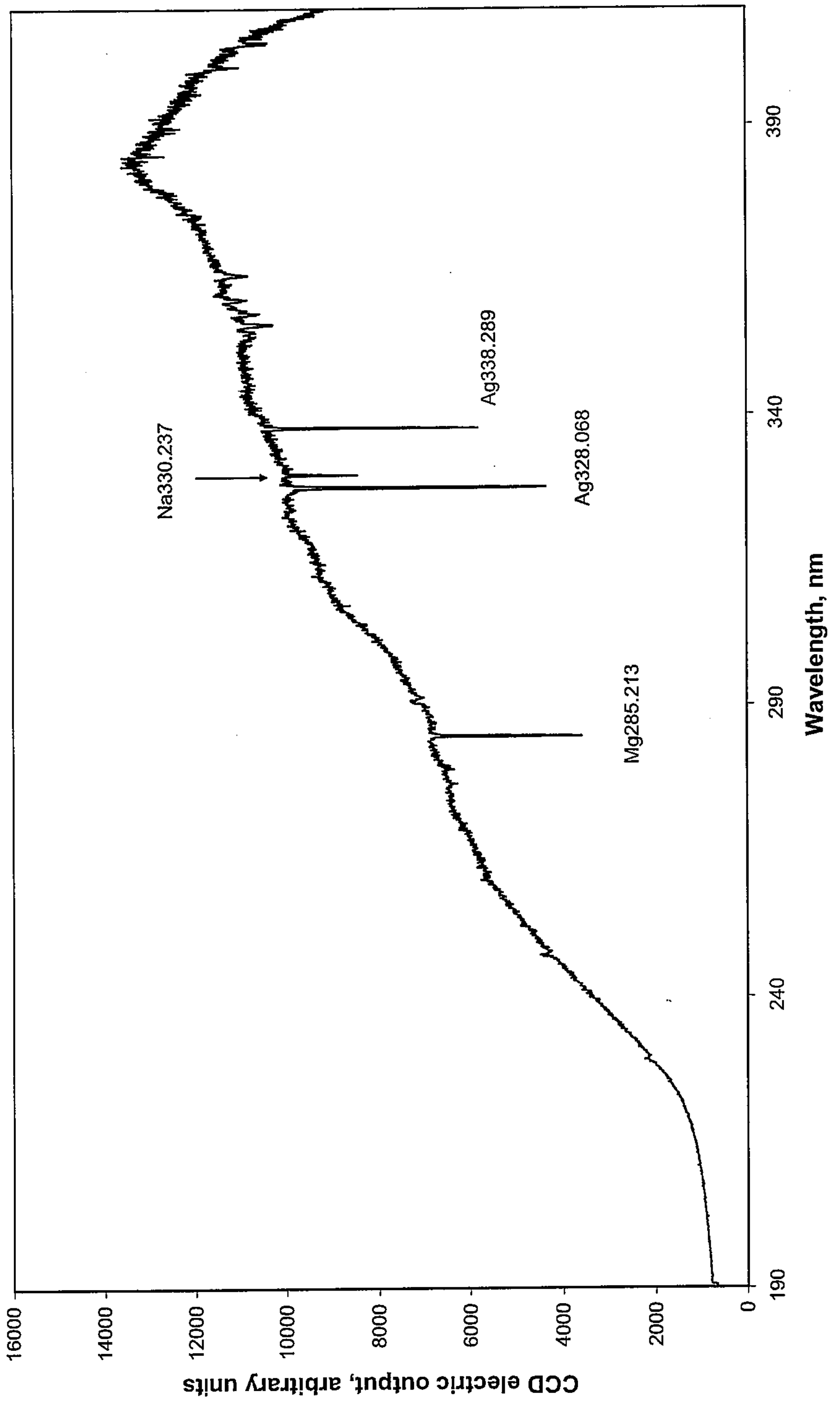
CCD electric output, arbitrary units
16000
14000
12000
10000
8000
6000
4000
2000
0
190
240
290
340
390
Wavelength, nm
Na330.237
Ag338.289
Ag328.068
Mg285.213

FIG. 3

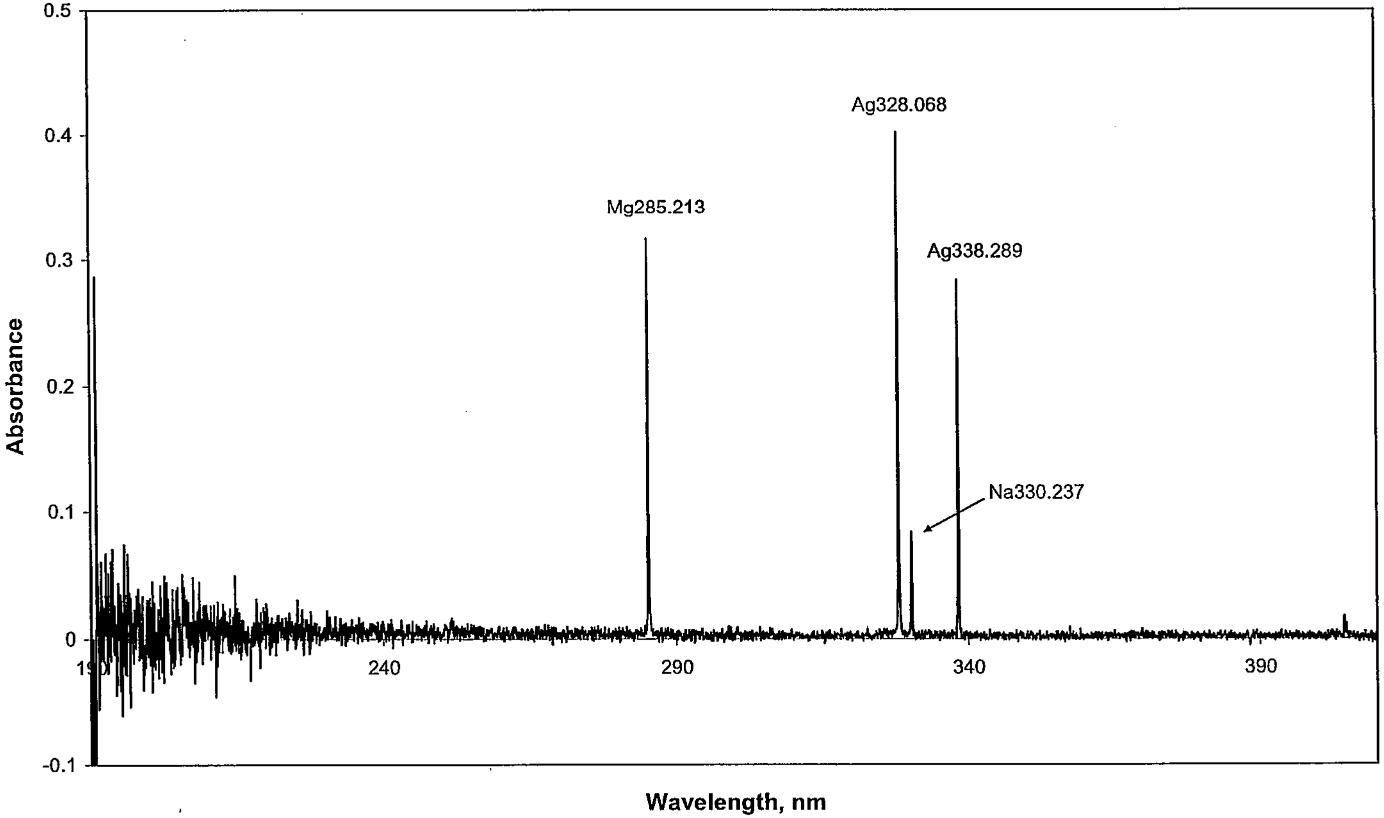
0.5
0.4
0.3
0.2
0.1
0
-0.1
Absorbance
190
240
290
340
390
Wavelength, nm
Mg285.213
Ag328.068
Ag338.289
Na330.237

FIG. 4

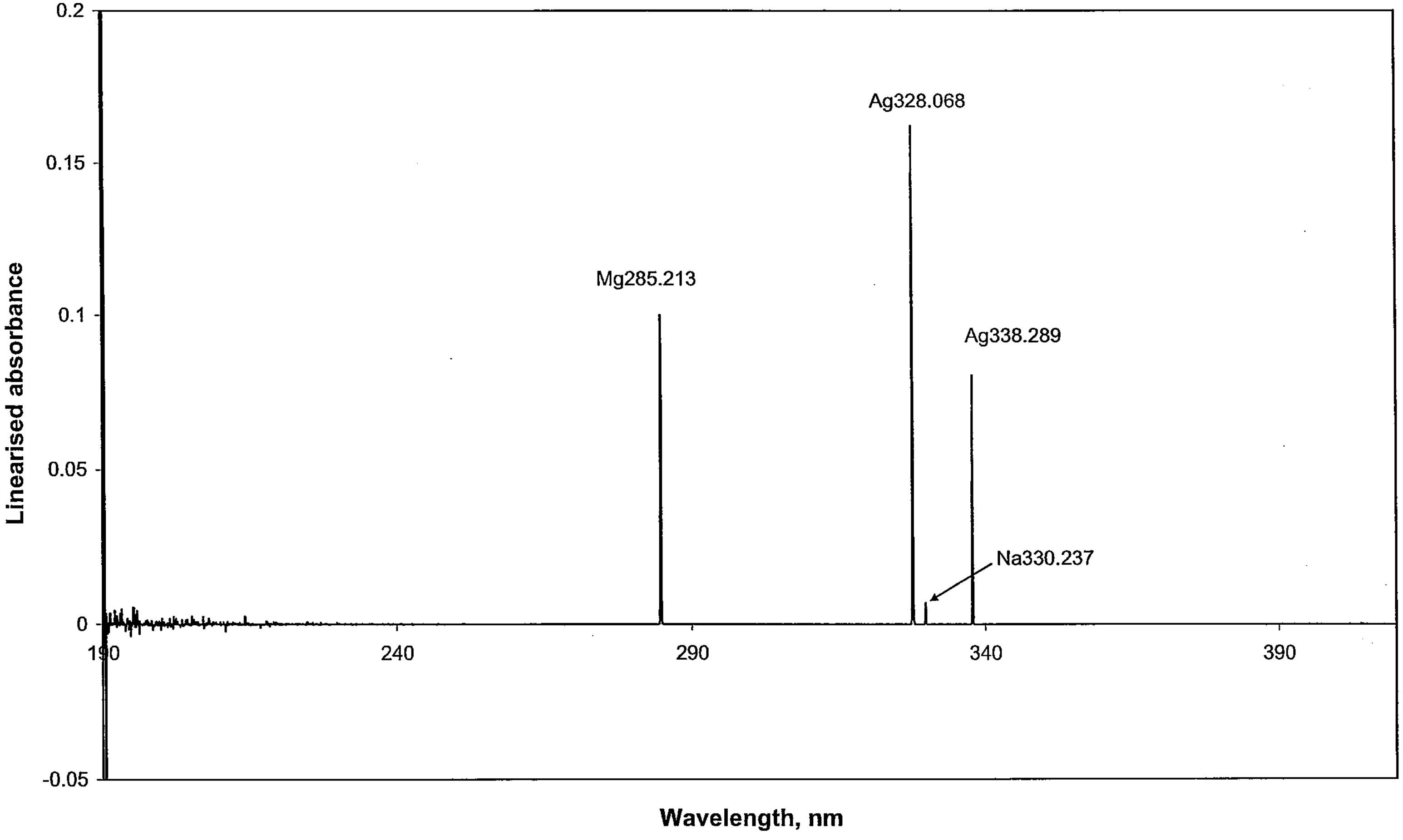
0.2
0.15
0.1
0.05
0
-0.05
Linearised absorbance
190
240
290
340
390
Wavelength, nm
Mg285.213
Ag328.068
Ag338.289
Na330.237

FIG. 5

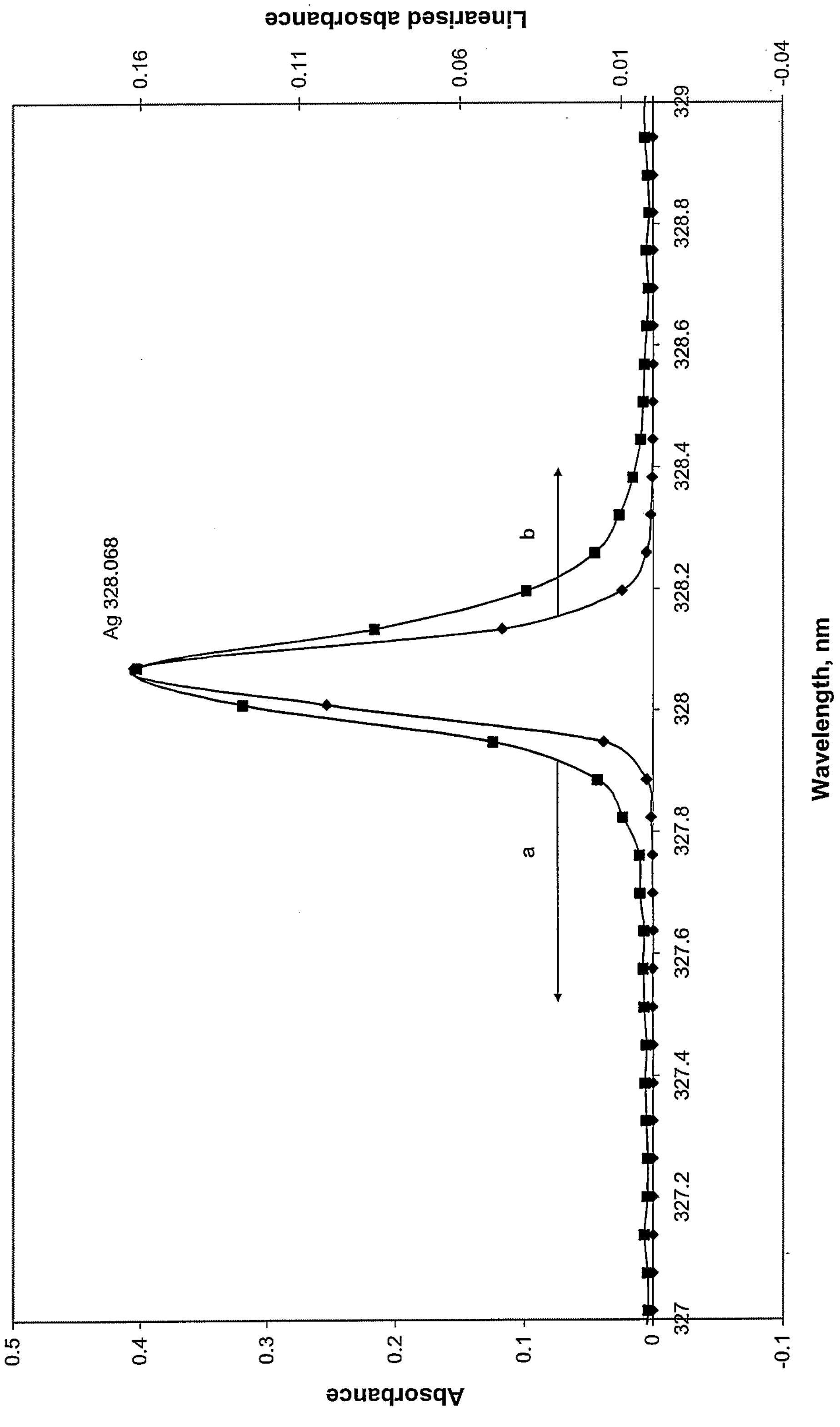
Linearised absorbance
0.16
0.11
0.06
0.01
-0.04
Ag 328.068
a
b
Absorbance
0.5
0.4
0.3
0.2
0.1
0
-0.1
327
327.2
327.4
327.6
327.8
328
328.2
328.4
328.6
328.8
329
Wavelength, nm

FIG. 6

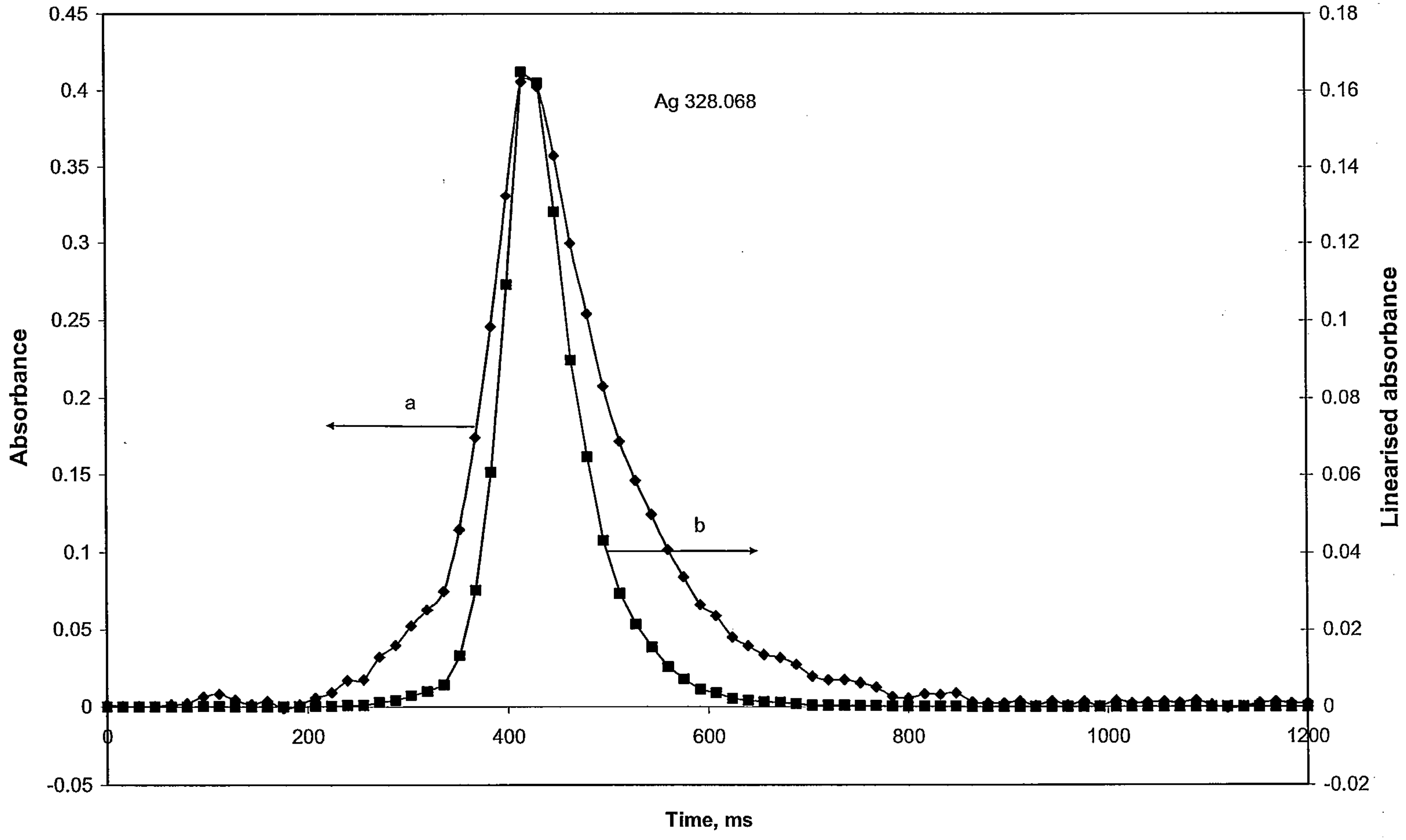
Ag 328.068
Absorbance
Linearised absorbance
Time, ms
a
b
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
0
200
400
600
800
1000
1200

FIG. 7

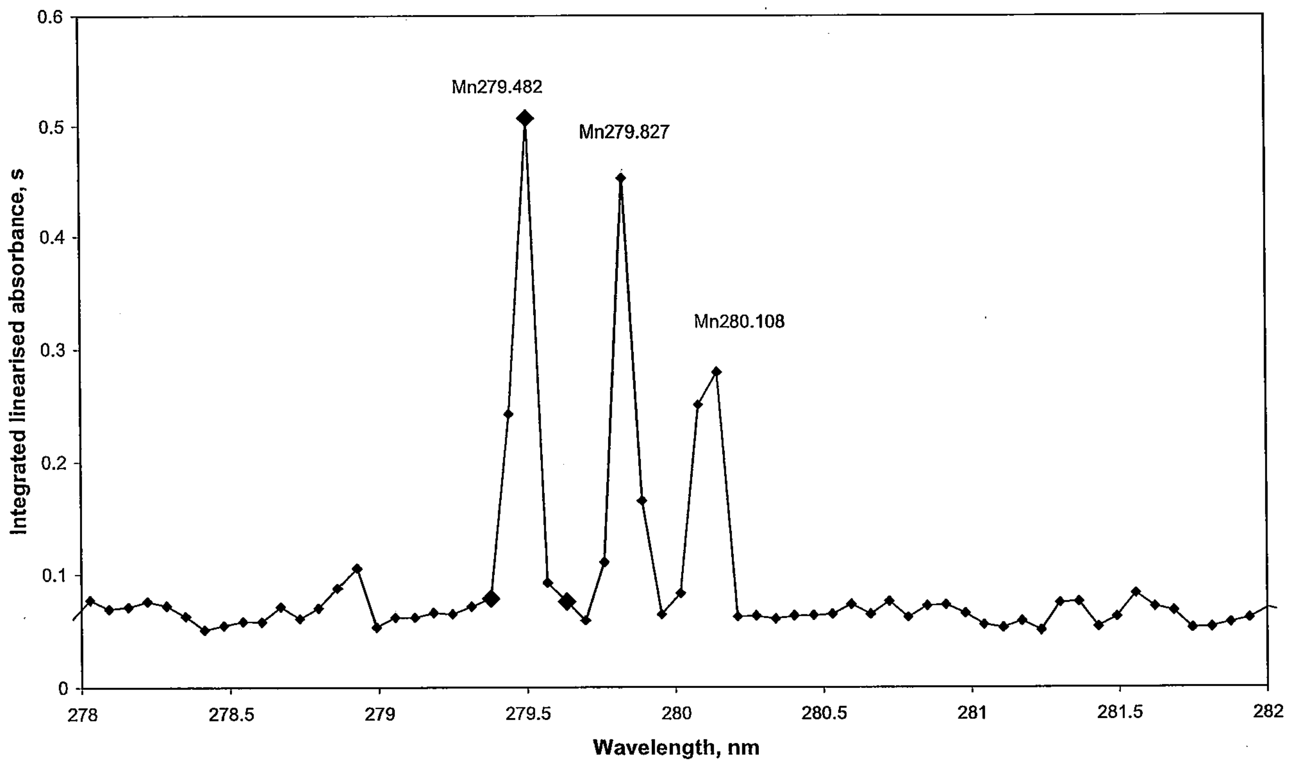
Integrated linearised absorbance, s
0.6
0.5
0.4
0.3
0.2
0.1
0
278
278.5
279
279.5
280
280.5
281
281.5
282
Wavelength, nm
Mn279.482
Mn279.827
Mn280.108

FIG. 8

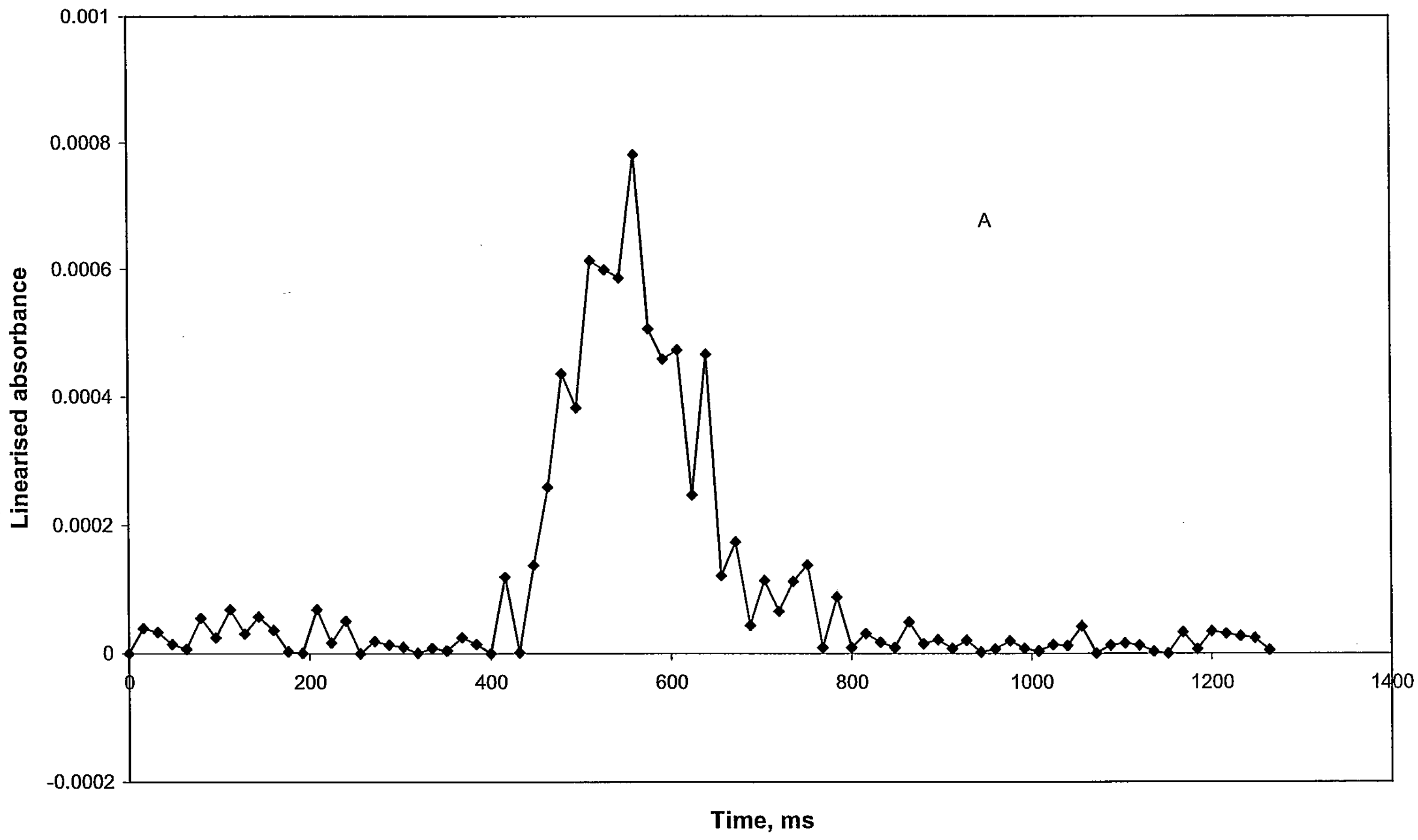
0.001
0.0008
0.0006
0.0004
0.0002
0
-0.0002
Linearised absorbance
A
0
200
400
600
800
1000
1200
1400
Time, ms

FIG. 9A

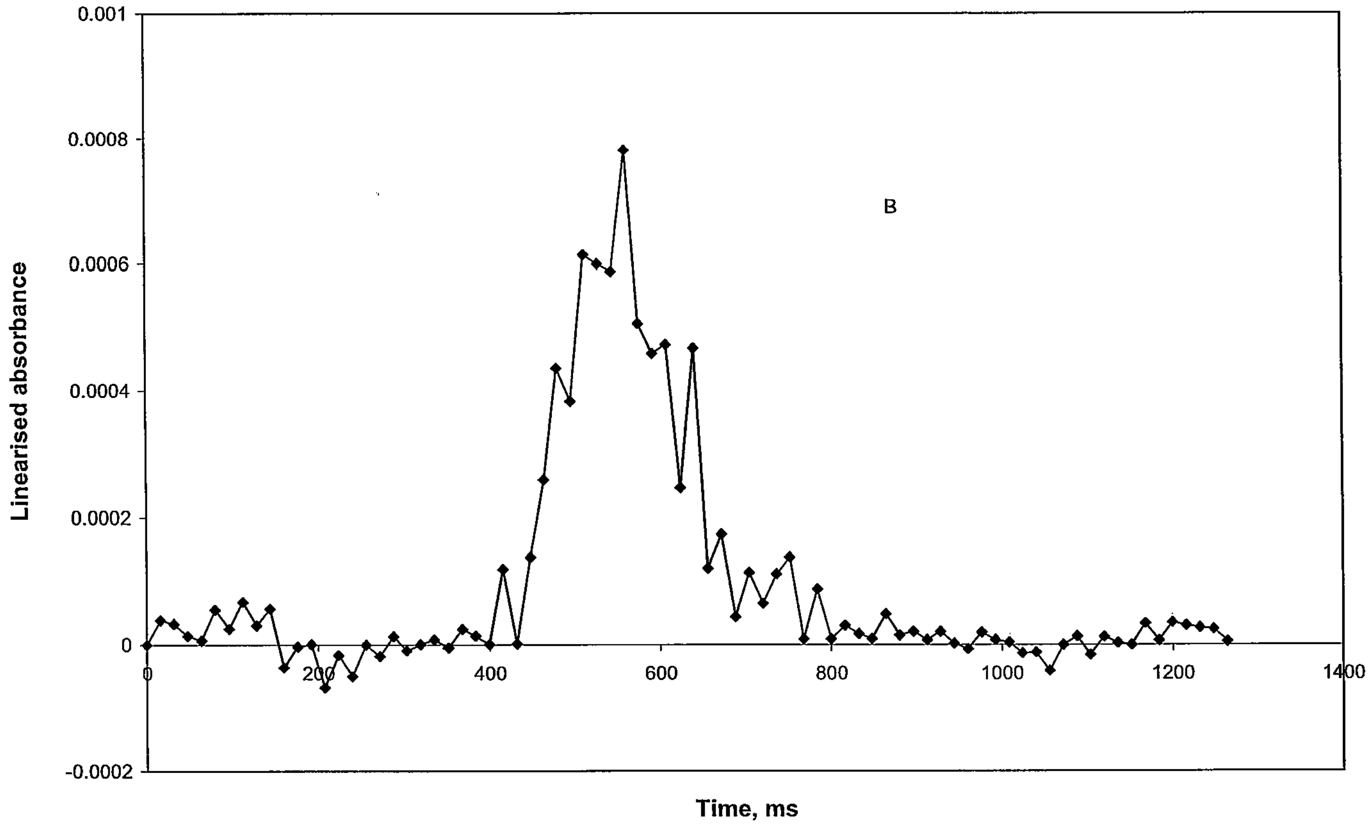
B
Linearised absorbance
0.001
0.0008
0.0006
0.0004
0.0002
0
-0.0002
0
200
400
600
800
1000
1200
1400
Time, ms

Fig. 9B

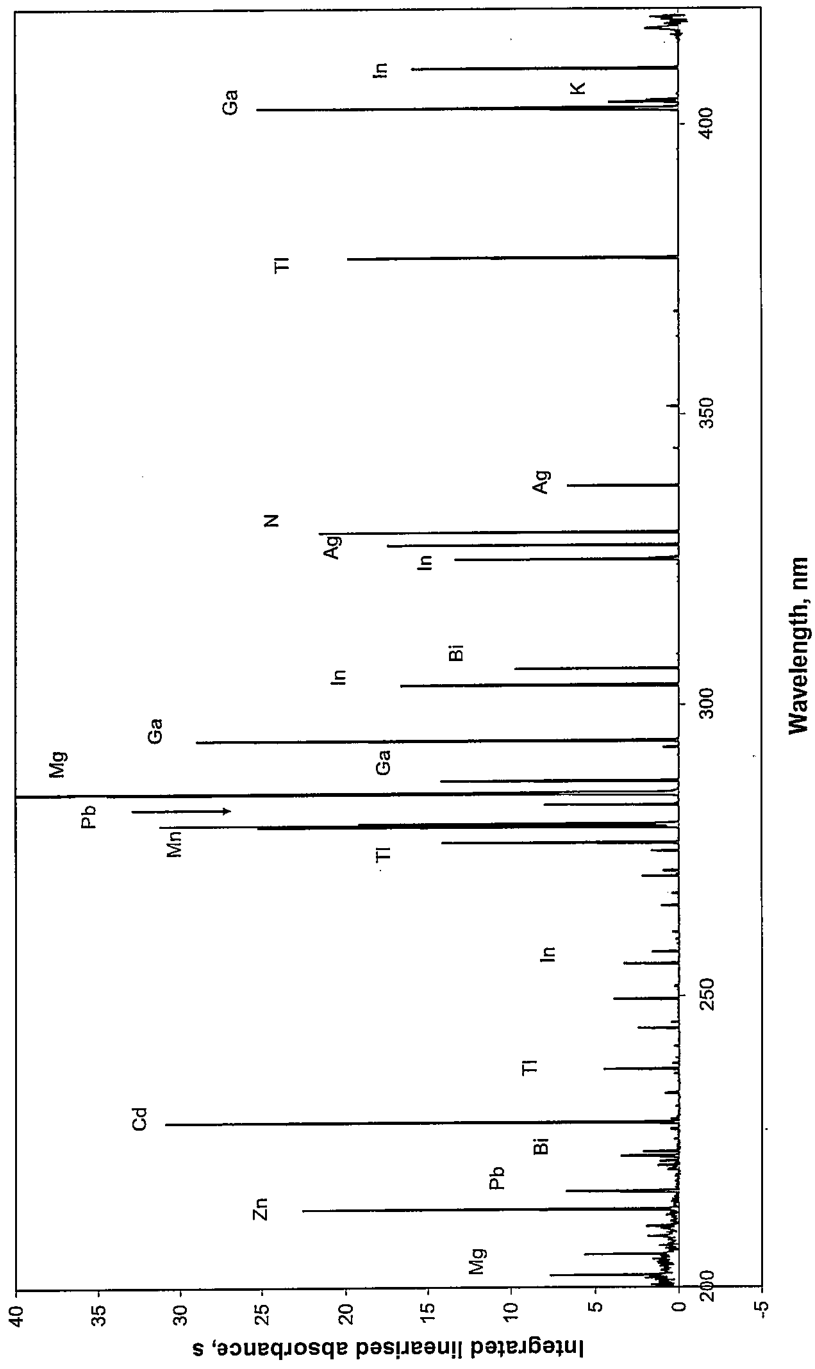
Integrated linearised absorbance, s
40
35
30
25
20
15
10
5
0
-5
200
250
300
350
400
Wavelength, nm
Mg
Zn
Pb
Bi
Cd
Tl
In
Tl
Mn
Pb
Mg
Ga
Ga
In
Bi
In
Ag
N
Ag
Tl
Ga
K
In

FIG.10

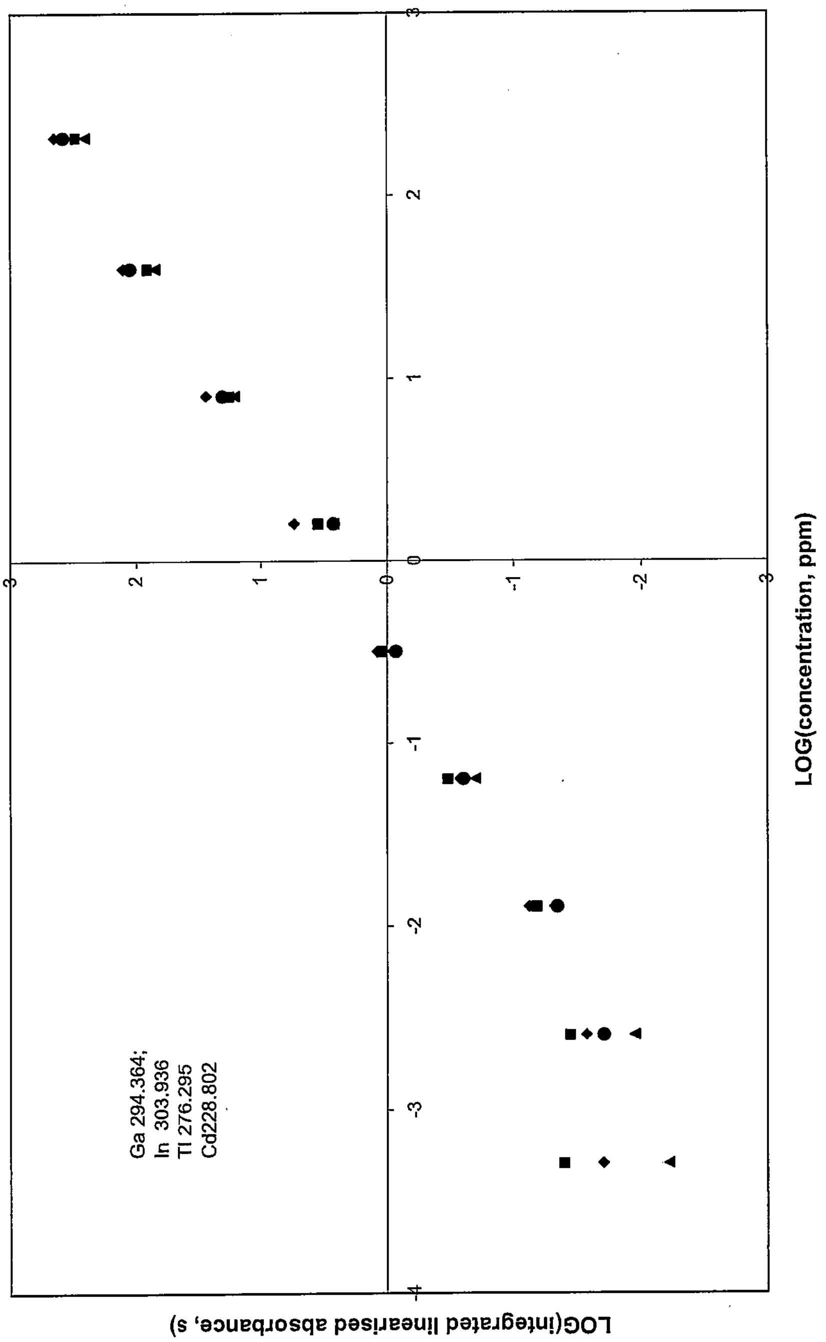
Ga 294.364;
In 303.936
Tl 276.295
Cd228.802
-4
-3
-2
-1
0
1
2
3
LOG(concentration, ppm)
-3
-2
-1
0
1
2
3
LOG(integrated linearised absorbance, s)

FIG.11

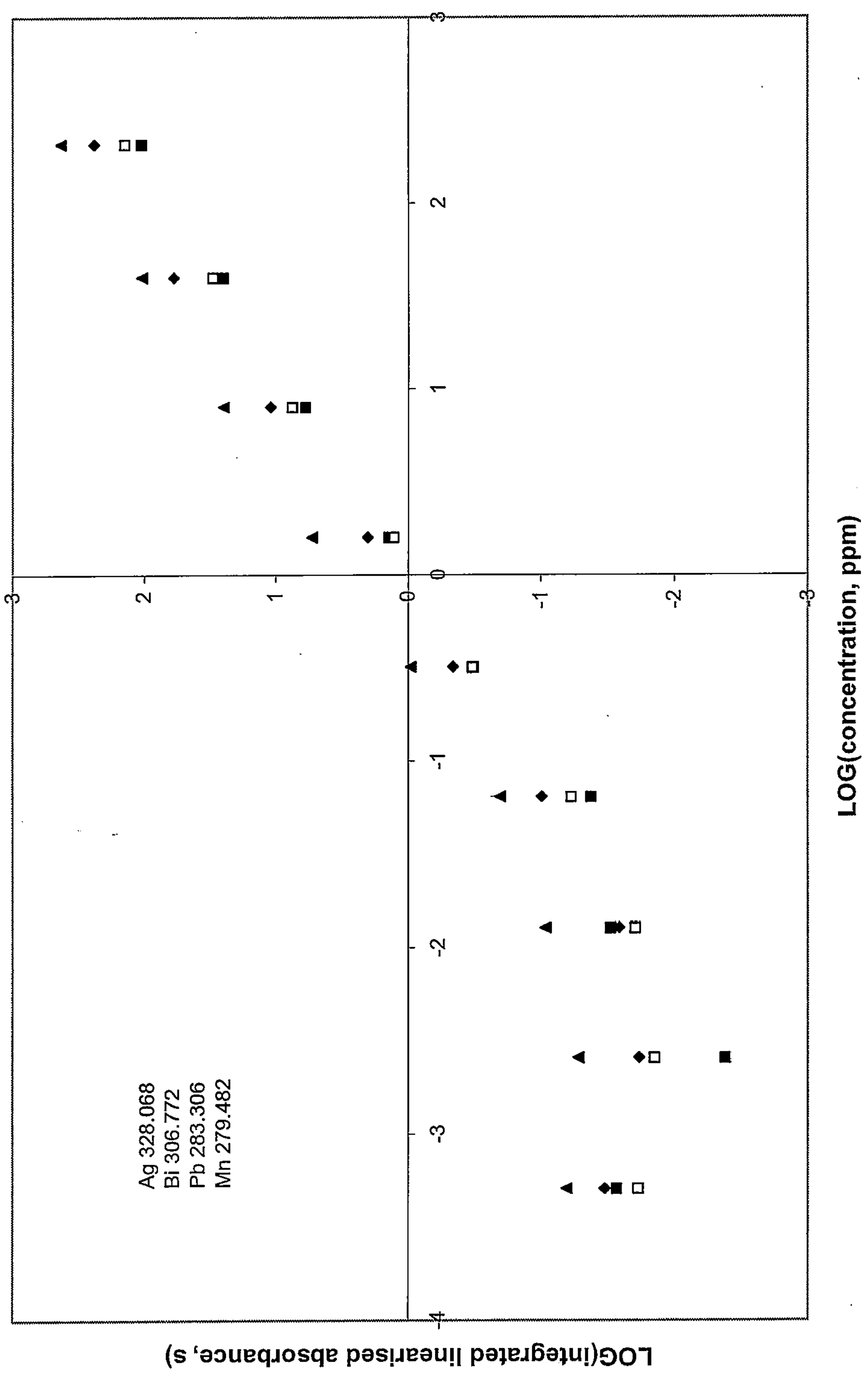
Ag 328.068
Bi 306.772
Pb 283.306
Mn 279.482
LOG(concentration, ppm)
LOG(integrated linearised absorbance, s)
-4
-3
-2
-1
0
1
2
3
-3
-2
-1
0
1
2
3

FIG. 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/050138

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/31 G01N21/74

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)
G01N G01J

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SCHUETZ M ET AL: "Continuum source-atomic absorption spectrometry using a two-dimensional charge coupled device" SPECTROCHIMICA ACTA. PART B: ATOMIC SPECTROSCOPY, NEW YORK, NY, US, US, vol. 55, no. 12, 15 December 2000 (2000-12-15), pages 1895-1912, XP007908610 ISSN: 0584-8547 * sections 1., 2.1, 3.2, 3.3 * ----- -/--	1-11, 14-20,22

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"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

"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

"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

"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 26 May 2009	Date of mailing of the international search report 03/06/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Spott, Thorsten

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/050138

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HARNLY JAMES M: "Future of atomic absorption spectrometry: A continuum source with a charge coupled array detector" JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY, ROYAL SOCIETY OF CHEMISTRY, CAMBRIDGE, GB, vol. 14, no. 2, 1 February 1999 (1999-02-01), pages 137-146, XP007908568 ISSN: 0267-9477 cited in the application * Introduction *	1-11, 14-20,22
A	* page 138, right hand col., first paragraph *	12,13,21
X	WELZ B ET AL: "High-Resolution Continuum-Source Atomic Absorption Spectrometry What Can We Expect?" JOURNAL OF THE BRAZILIAN CHEMICAL SOCIETY, SAO PAULO, BR, vol. 14, no. 2, 1 March 2003 (2003-03-01), pages 220-229, XP007908579 ISSN: 0103-5053 the whole document	1-11, 14-20,22
A	US 3 565 567 A (RAINS STEPHEN D) 23 February 1971 (1971-02-23) * col. 4, lines 43-75; col. 8, lines 16-49 *	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2009/050138

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			AU	2981492	A	10-06-1993
			DE	4240301	A1	09-06-1993
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			JP	3325937	B2	17-09-2002
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