(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 068 516 B9**

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**
Note: Bibliography reflects the latest situation

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see page(s) 15

(48) Corrigendum issued on:
07.01.2004 Bulletin 2004/02

(45) Date of publication and mention
of the grant of the patent:
21.05.2003 Bulletin 2003/21

(21) Application number: **99915670.6**

(22) Date of filing: **18.03.1999**

(51) Int Cl.^{7}: **G01N 21/71**

(86) International application number:
PCT/EP1999/001842

(87) International publication number:
WO 1999/049301 (30.09.1999 Gazette 1999/39)

(54) METHOD FOR QUANTITATIVE ANALYSIS OF ATOMIC COMPONENTS OF MATERIALS BY LIBS SPECTROSCOPY MEASUREMENTS

VERFAHREN ZUR QUANTITATIVEN ANALYSE VON ATOMAREN MATERIALBESTANDTEILEN DURCH LIBS SPEKTROSKOPIE

PROCEDE D'ANALYSE QUANTITATIVE DES CONSTITUANTS ATOMIQUES DE MATERIAUX AU MOYEN DE MESURES SPECTROSCOPIQUES LIBS

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: **20.03.1998 IT PI980023**

(43) Date of publication of application:
17.01.2001 Bulletin 2001/03

(73) Proprietor: **CONSIGLIO NAZIONALE DELLE RICERCHE**
00185 Roma (IT)

(72) Inventors:
- **PALLESCHI, Vincenzo**
  I-56124 Pisa (IT)
- **CIUCCI, Alessandro**
  I-57100 Livorno (IT)
- **RASTELLI, Simone**
  I-51010 Massa e Cozzile (IT)
- **TOGNONI, Elisabetta**
  I-56126 Pisa (IT)

(74) Representative: **Mittler, Enrico**
c/o Mittler & C. s.r.l.,
Viale Lombardia, 20
20131 Milano (IT)

(56) References cited:
WO-A-97/15811

- **GODDARD B J: "Materials analysis using laser-based spectroscopic techniques" TRANSACTIONS OF THE INSTITUTE OF MEASUREMENT AND CONTROL, 1991, UK, vol. 13, no. 3, pages 128-139, XP000241982 ISSN: 0142-3312**
- **SONG K ET AL: "APPLICATIONS OF LASER-INDUCED BREAKDOWN SPECTROMETRY" APPLIED SPECTROSCOPY REVIEWS, vol. 32, no. 3, 1 August 1997 (1997-08-01), pages 183-235, XP000774246 ISSN: 0570-4928**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 068 516 B9

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a method for quantitative analysis of atomic components of materials by LIBS spectroscopy measurements without calibration.

[0002] Quantitative and real time analysis of the elementary composition of materials is of great interest in many fields, from industrial production to environment diagnostics, from on-line control of product quality to monitoring of industrial exhausts.

[0003] At present, the most widespread systems of quantitative analysis require sampling of the materials, with a consequent off-line characterisation. Generally, this procedure involves an increase of the times for the acquisition of the necessary data and, therefore, of costs and risks.

[0004] LIBS (*Laser Induced Breakdown Spectroscopy*) or LIPS (*Laser Induced Plasma Spectroscopy*) technique is a technique for quick analysis of sample's elementary constituents, that can be applied in situ and gives results in real time. Current systems based on LIBS relay of calibration curves in order to determine the concentration of the various elements [D.A. Cremers, M.J. Ferris and M. Davies: *"Transportable Laser Induced Breakdown Spectroscopy (LIBS) instrument for field-based soil analysis*". SPIE Vol. 2835 (190-200) 1996].

[0005] The article of B. J. Goddard "Materials analysis using laser-based spectroscopic techniques", Transaction of the Institute of Measurement and Control, 1991, UK, vol. 13, no. 3, pages 128-139, discloses several laser based spectroscopic methods capable of detecting low concentrations of a particular element. In the case of a LIBS methods, for a system in LTE it is possible to derive the relative concentrations of the elemental constituents by measuring line intensities.

[0006] The patent application WO 97/15811 relates to spectroscopic determination of the concentration of atomic species in samples. The concentration of the atomic species to be determined is then derived from the known emission intensity of a predetermined concentration of that specie in the sample at the measured temperature, a quantity which would have been measured prior to the determination of the unknown concentration, and the actual measured emission from the unknown species, or by this latter emission and the emission intensity of a species having known concentration within the sample such as nitrogen for gaseous air samples.

[0007] The present invention proposes a method and a system based on LIBS technology, for determining the concentration of the various elements present in a sample, without the use of calibration curves.

[0008] The method and the system of the present invention are defined in the independent claims 1 and 14, respectively, and particular embodiments of said method are defined in the dependent claims.

[0009] The application of the present method allows:

i) to perform quantitative analysis by the LIBS technique, without need of reference samples, and without calibrations;
ii) to reduce measurement costs and times, because the method is self-consistent (the experimental quantities that are necessary to determine the concentrations are absolute quantities that are obtained from the same measure).

[0010] The invention is described herein, with illustrative and non-limiting purpose, for some applications that are considered as being particularly significant.

a) Working principle of the LIBS technique

[0011] LIBS is based on the analysis of the spectrum of the radiation emitted by the atoms of the sample, when they are excited and ionised by a laser pulse that is properly focused on the target.

[0012] The beam of a pulsed laser is focused on a sample through an appropriate optical system. If the energy of the laser pulse is sufficiently high, the density of photons in the focal spot is such as to trigger multiphotonic ionisation. (even if the phenomenon has a very low probability). The first free electrons are accelerated by the electric field of the radiation and they ionise other atoms by impact; a chain reaction which produces the breakdown, with its characteristic detonation noise and flash of light, is thus generated. The plasma (composed of neutral atoms, ions and free electrons), which is formed in the first instants of the laser pulse, absorbs energy from the laser pulse, thus reaching temperatures of the order of about ten eV ($\sim 10^5$ K) ($\sim 10^5$ °C). The material contained in the focal spot (characteristic volume ~ 0.1 mm^3) is thus heated and ionised. Once the pulse and heating phase are over, the plasma cools down and the atomic species generate their specific spectrum. By resolving the evolution of plasma through time, it is possible to discriminate various radiation regimes:

a) *bremsstrahlung* radiation;
b) emission of the spectrum lines of the elements;

c) emission of vibration bands of simple molecules, formed as a consequence of the impacts.

[0013] LIBS analysis is based on the measurement of the lines indicated at point b). To this purpose, the observation of the spectrum must start with a certain delay with respect to the laser pulse, in order to reduce the effects of the presence of *bremsstrahlung* radiation. The typical working regime thus individuated corresponds to plasma temperatures of the order of 1 eV (~ 10^4 °C). The duration of the observation is established on the bases of the characteristics of the apparatus (energy and duration of the laser pulse) in order to maximise the signal/noise ratio and to limit the temperature variations due to the dynamics of plasma.

[0014] In the case in which during the time interval of observation the condition of LTE (*Local Thermal Equilibrium*) [*"Principles of Laser Plasma*" Ed. by G. Bekefi. J. Wiley & Sons, 1976] is verified, the plasma is characterised by its temperature and by the electronic density.

[0015] The atomic elements that form the plasma are present in different ionisation states. It is called species herein an element having a certain ionisation state (e.g.: neutral magnesium [MgI] and ionised magnesium [MgII] are two species of the same element). In the case of LTE, the population of the atomic levels is described by Boltzmann distribution; the ratio between populations of two levels belonging to subsequent ionisation states of a same element is given by Saha-Boltzmann equation:

$$\frac{N_e N_1(Z)}{N_n(Z-1)} = 6.0\times10^{21}\,\frac{g_1^Z T_e^{3/2}}{g_n^{Z-1}}\exp\left(-E_\infty^Z(n,\ell)\Big/T_e\right), \qquad (1)$$

where:

N_e: electronic density (cm^{-3});
N_n (Z-1): level *n* population, of the species with (Z-1) charge;
$N_l(Z)$: fundamental level population, of the species with (Z) charge;
g_l^Z: degeneration of the fundamental level of the species with (Z) charge;
g_n^{Z-l}: degeneration of the n level of the species with (Z-1) charge;
$E_\infty^Z(n, \ell)$: ionisation energy of the (Z-1) charge species initially at level (n, ℓ);
T_e: electronic temperature of plasma.

[0016] T_e, which appears in equation 1, is the temperature of the distribution of the free electrons in the plasma; while *T* plasma temperature stands for temperature of the bonded electrons. In working condition (LTE), the difference between these temperatures is negligible.

[0017] The intensity of each spectral line, characteristic of each species *a* present in the plasma, depends on the concentration of the same species N_a and on the population of the starting level, that is on the plasma temperature *T*, according to the formula:

$$I_{ki}^{\lambda} = N_a\,\frac{g_k \exp\left(-E_k\Big/k_B T\right)}{U_a(T)}\,A_{ki} \qquad (2)$$

where I_{ki}^{λ} is the number of photons emitted per volume unit and for time unit at the wavelength λ, characteristic of the transistion between the levels *k* and *i* of the species *a*, g_k is the degeneration of the upper level, E_k the energy of the upper level, k_B the Boltzmann constant, A_{ki} the probability of transition between the two levels *k* and *i*, $U_a(T)$ the partition function of the species *a* at the temperature *T*, according to the expression:

$$U_a(T) = \sum_k g_k \exp\left(-E_k\Big/k_B T\right) \qquad (3)$$

b) Procedure for the analysis at the base of the proposed method

[0018] The value of the quantity T is obtained through measurements of the intensity of the radiation emitted by electronic transitions.

[0019] The measured intensity values, $\bar{I}^{\lambda}_{ki}$, are connected with the emitted intensity, I^{λ}_{ki}, by a proportion factor F, depending on the experimental apparatus and on the measurement conditions (the spectral response of the experimental apparatus is evaluated in the calculation of the quantity $\bar{I}^{\lambda}_{ki}$).

[0020] Such factor F must be constant during a measurement run, that is the acquisition of all the portions of spectrum that are necessary to the measurement must be taken under the experimental conditions.

[0021] Therefore the following relation is valid:

$$\bar{I}^{\lambda}_{ki} = FI^{\lambda}_{ki} \qquad (4)$$

[0022] By utilising the measured values of the intensity of the lines emitted by a same species and the relative spectroscopic data (E_k, g_k, A_{ki}, that are available in literature), it is possible to calculate the temperature of the plasma. By substituting in eq. 4 the expression I^{λ}_{ki}, from equation 2, and by taking the natural logarithm of both terms the result is:

$$\ln\frac{\bar{I}^{\lambda}_{ki}}{g_k A_{ki}} = \ln\frac{FN_a}{U_a(T)} - \frac{E_k}{k_B T} \qquad (5)$$

[0023] In the LTE condition, the temperature T is the same for all species and $U_a(T)$ is determined by the temperature. Equation 5 is therefore the equation of a straight line:

$$y_{ki} = m + nx_{ki} \qquad (6)$$

where:

$x_{ki} = E_k$
$y_{ki} = \ln(\bar{I}^{\lambda}_{ki} / g_k A_{ki})$
$m = \ln(FN_a / U_a(T))$
$n = -1 / k_B T$

[0024] For each species, the values (x_{ki}, y_{ki}) which characterise each line are reported on the plane (E, $\ln(\bar{I}/gA)$): for each species the value of the slope n and of the intercept m is obtained by linear regression. The slope n thus obtained gives the value of the temperature of the plasma:

$$T = -1 / k_B n. \qquad (7)$$

[0025] With the value T calculated through equation 7 (possibly averaged on the different species), the value of the $U_a(T)$ is determined through equation 3. At this point, by using the intercept value m, it is possible to calculate the value of the concentration FN_a, that is the product of the concentration of the species a times the experimental factor F.

[0026] In this way, one proceeds to the measurement of FN_a for all the species that have been identified (Note: once T has been found, the measure of a single line will be sufficient to determine FN_a).

[0027] In working conditions ($T \sim 1$ eV) ($\sim 10^4$ °C), only spectra that are emitted by the first two species of each element, that is by the neutral state and by the first ionisation one, are observed: indeed, the relative abundance of atoms in states of ionisation above the first is lower than 10^{-3}.

[0028] Once the plasma temperature and the species concentrations (times the F Factor) have been obtained, the concentration of the elements (hereinafter indicated by C_i) can be calculated.

[0029] The procedure is done according to the following scheme:

A) Calculation of the concentrations of the elements times the experimental factor F.

[0030] For each element the following cases can be encountered:

i) the concentrations FN_a for both species are available: then the concentration of the element is obtained through the sum of the concentrations of the two species. In addition, through eq. 1, it is possible to calculate N_e (that in this case is the only unknown quantity). Then, the procedure continues according to point B)

ii) the concentration for only one of the two species is available and the value N_e is known (this case occurs when there is at least one element for which the concentrations of both species have been measured): the concentration of the element can be obtained by calculating the concentration of the other species, through eq. 1, and by summing the concentrations of the two species. Then, the procedure continues according to point B)

iii) the concentrations for only one of the two species is available and the value N_e is not known (this case occurs when it is possible to measure the lines of a single species for each one of the identified element): in this case N_e is calculated as value of convergence of an iterative algorithm based on Saha equation and on the concentrations of the species that have been individuated. That is, a reasonable starting value for N_e must be set (in the typical working conditions $N_e \sim 10^{18}$ electrons/cm^3) and then the procedure continues according to point ii) for the determination of the concentrations of the elements, times the F factor; then it is necessary to proceed with the calculation of the real concentrations according to point B). Once the F factor has been eliminated and the concentrations of the elements have been obtained, N_e is recalculated as the sum of the concentrations N_i of the ionised species (for the neutrality condition of plasma this corresponds to:

$$N_e = \sum_{i=1}^{Tot} N_i(\mathrm{II}),$$

where *Tot* is the number of individuated elements). This new value of N_e is reintroduced at point iii) of the algorithm and the cycle is repeated until the value of N_e converges.

B) Determination of the experimental factor F and calculation of the real concentrations.

[0031] It is possible to proceed in two ways:

i) to utilise an internal reference. When the concentration $C_{element}^{known}$ of an element of the sample is known (e.i. Nitrogen in atmosphere), it is possible to determine the factor F as the ratio between the concentration of the same element, as measured with the LIBS method according to point A), and the known concentration

$$F = \frac{(FC_{element})LIBS}{C_{element}^{known}}, \tag{8}$$

and then to rescale the other concentrations with the value F, thus determined;

ii) to normalise each concentration with respect to the sum of all concentrations:

$$C_i = \frac{(FC_i)_{LIBS}}{\sum_{j}^{Tot}(FC_j)_{LIBS}}, \tag{9}$$

where *Tot* indicates the number of individuated elements. The concentrations calculated according the methods described in point ii) are affected by a percentage error that is equal to at least the concentration of the elements that have not been individuated. The measurements taken according to the method described in point i) are affected only by a percentage error that is determined by the precision by which the reference is known, but such method is only applicable when an internal reference is available.

[0032] The algorithm described in points A) and B) is summarised in the flow chart shown in Figure 6.

[0033] A block scheme describing the procedure for the quantitative analysis herein presented, is shown in Figure 7.

Description of possible applications:

[0034] There are described hereinafter different applications of the LIBS technique here described. In all applications the same spectrum analysis procedure that is described in the previous block scheme is utilised.

a) Characterisation of metal alloys

[0035] In the characterisation of metal alloys the interest is usually on the measurement of the concentration of the major components, that is of the components that are present in percentage that is at least 0.1%. In other cases it can otherwise be important to determine the presence of impurities in the alloys, in a quick way, giving priority to measurement sensitivity rather than accuracy.

[0036] A suitable apparatus is shown in Fig. 1 and consists of a laser radiation source 1, a focusing optic system 2, a first mirror 3, a support 4 for a metal alloy sample 5, a second mirror 6, an optic system 7 for receiving the emitted signal, an optic fibre 8, a spectrometer 9, a timing system 10 for discriminating the spectrum lines from the continuous emission, a computer 11, an electronic control and interfacing system 12 and a software for analysis of data.

[0037] For the analysis of metal alloys, typical working conditions are:

- density of laser radiation flow on the target: $\sim 10^8$ Wcm^{-2}
- repetition rate of 10 Hz
- reception with quartz optics (transparent to UV)
- use of a system for the movement of the sample to control the irradiated spot.

b) Monitoring of trace elements in the atmosphere

[0038] In the analysis of traces in the atmosphere the interest is on the measurement of pollutans or other elements that are present in the form of aerosol, submicrometric particulate or vapours, in quantities in the order of ppm.

[0039] A suitable apparatus is shown in Figure 2 and consists of a laser radiation source 21, a focusing optic system 22 for directing the laser radiation in the gas, an optic system 24, an optic fibre 25, a spectrometer 26, a timing system 27 for discriminating the spectrum lines from the continuous emission, a computer 28, an electronic control and interfacing system 29 and a software for analysis of data.

[0040] For the monitoring of the elements present in traces in the atmosphere, typical working conditions are:

- density of laser radiation flow at the focal spot: $\sim 5.10^9$ Wcm^{-2}
- repetition rate of 10 Hz (or greater)
- reception with quartz optics (transparent to UV).

c) Analysis of soils

[0041] A suitable apparatus for carrying out fast in situ or laboratory analysis of soils with the method according to the invention is shown in Fig. 3 and comprises a laser radiation source 31, a mirror 32 for directing the laser radiation towards on a soil sample 33 on a support 34, a focusing lens 35, a collecting optics 37, an otical fibre 38, an optical signal analysing system 39, a computer 40 and a software for analysis of data.

d) Analysis of cultural heritage

[0042] A suitable apparatus for carrying out the analysis of cultural heritage with the method according to the invention is shown in Fig. 4 and comprises a laser radiation source 41, a frequency multiplier 42, a group of four mirrors 43-46 for selectively directing the laser radiation towards a target 47 either directly (LIPS analysis) or through a frequency multiplier [for LIF (*Laser Induced Frequency*) analysis], two further mirrors 48-49 for directing the emitted signsl towards a sensor 50, a computer 51 and a software for analysis of data.

e) Atomic emission spectroscopy

[0043] A suitable apparatus for carrying out atomic emission spectroscopy with the method according to the invention is shown in Fig. 5 and comprises a sample 61 on whose surface a plasma 62 is generated by a laser source or any other radiation source such as electric spark, microwaves and so on. The emitted signal reaches a dispersion reticule 63 inside a housing 64 provided with a plurality of slits 65, each faced to a respective photomultiplier 66. The photomultipliers collect the integral line intensity corresponding to specific emission lines of the materials, and these data are processed using the spectral analysis procedure here described.

Claims

1. Method for quantitative measurement of the concentration of atomic components of solid, liquid or gaseous materials, comprising:

a) spectral analysis of the radiation, emitted by a sample including a plurality of elements excited and ionised in such a way to generate a plasma;
b) qualitative analysis of the emitted radiation;
c) quantitative analysis without calibration of the emitted radiation, wherein said quantitative analysis includes:
d) measuring the intensity of the spectral lines emitted by each element;
e) obtaining the plasma temperature (T) from at least one species of the emitted radiation;
characterized by
f) determining the concentration (N_a) of all the species multiplied by a proportion factor (F);
g) calculating the concentration of each element as sum of the corresponding species concentrations;
h) normalising each concentration with respect to the sum of all concentrations, in order to eliminate said proportion factor (F).

2. Method according to claim 1, **characterized in that** said temperature (T) is determined making an average between measures of more than one species.

3. Method according to claim 1, **characterized in that** further comprises the step of determining the value of the electronic density (N_e).

4. Method according to claim 3, **characterized in that** if the concentration (FN_a) for only one of the species is available the concentration of the other species is calculated by means of the Saha-Boltzmann equation.

5. Method according to claim 1, **characterized in that** if the concentration (FN_a) for only one of the species is available and the value of the electronic density (N_e) is not known the concentration of the other species is calculated as value of convergence of an iterative algorithm based on Saha-Boltzmann equation and on the concentrations of the species that have been individuated.

6. Method according to claim 5, **characterized in that** said iterative algorithm comprises the step of:

a) setting a starting value for the electronic density (N_e),
b) calculating the concentration of the other species by means of the Saha-Boltzmann equation,
c) normalising each concentration with respect to the sum of all concentrations, in order to eliminate said proportion factor (F),
d) calculating the electronic density (N_e) as the sum of the concentrations (N_i) of the ionized species,
e) reintroducing the value of the electronic density (N_e) in the calculation at the point b), and repeating the cycle until the value of the electronic density (N_e) converges.

7. Method according to claim 1, **characterized in that** said method comprises:

a) individuation of the spectral lines;
b) measurement of the wavelength at a mid line;
c) measurement of the line integral.

8. Method according to claims 1 or 7, **characterized in that** said method comprises identification of the species through correspondence between the wavelength measurement at mid line and proper database, according to the maximum probability criterion.

9. Method according to claim 1, **characterized by** its application for characterisation of metal alloys.

10. Method according to claim 1, **characterized by** its application for monitoring trace elements in the atmosphere.

11. Method according to claim 1, **characterized by** its application for in situ or laboratory analysis of soils.

12. Method according to claim 1, **characterized by** its application for analysis of cultural heritage.

13. Method according to claim 1, **characterized by** its application for atomic emission spectroscopy.

14. System for quantitative analysis of atomic components of materials including a plurality of elements by LIBS spectroscopy measurements comprising:

a) a laser radiation source (1);
b) optical means (2, 3) to direct the laser source radiation toward the material;
c) an optic system (7) for receiving the radiation emitted by the plasma generated by the material;
d) an optical signal analysing system (9);
e) a computer (11) including:

means for measuring the intensity of the spectral lines emitted by each element;
means for obtaining the plasma electron temperature (T) from at least one species of the emitted radiation;

characterized in that said computer further includes

means for determining the concentration (N_a) of all the species multiplied by a proportion factor (F);
means for calculating the concentration of each element as sum of the corresponding species concentrations;
means for normalising each concentration with respect to the sum of all concentrations, in order to eliminate said proportion factor (F).

Patentansprüche

1. Verfahren zur quantitativen Messung der Konzentration von atomaren Bestandteilen von festen, flüssigen oder gasförmigen Materialien, umfassend:

a) Spektralanalyse der Strahlung, die von einer Probe abgegeben wird, welche eine Vielzahl von Elementen enthält und in einer solchen Weise angeregt und ionisiert wird, dass ein Plasma erzeugt wird;

b) qualitative Analyse der abgegebenen Strahlung;

c) quantitative Analyse ohne Kalibrierung der abgegebenen Strahlung, wobei die quantitative Analyse beinhaltet:

d) Messen der Stärke der Spektrallinien, die von jedem Element abgegeben werden;

e) Erhalten der Plasmatemperatur (T) von zumindest einer Art der abgegebenen Strahlung;
gekennzeichnet durch

f) Bestimmen der um einen Verhältnisfaktor (F) multiplizierten Konzentration (N_a) aller Arten;

g) Berechnen der Konzentration jedes Elements als Summe der entsprechenden Artenkonzentrationen;

h) Normalisieren jeder Konzentration in Bezug auf die Summe aller Konzentrationen, um den Verhältnisfaktor (F) zu beseitigen.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Temperatur (T) durch Herstellen eines Durchschnitts zwischen Messungen von mehr als einer Art bestimmt wird.

3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** es ferner den Schritt des Bestimmens des Werts der Elektronendichte (N_e) umfasst.

4. Verfahren nach Anspruch 3, **dadurch gekennzeichnet, dass** dann, wenn die Konzentration (FN_a) für nur eine der Arten verfügbar ist, die Konzentration der anderen Arten durch die Saha-Boltzmann-Gleichung berechnet wird.

5. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** dann, wenn die Konzentration (FN_a) für nur eine der Arten verfügbar ist und der Wert der Elektronendichte (N_e) nicht bekannt ist, die Konzentration der anderen

Arten als Wert der Konvergenz eines iterativen Algorithmus beruhend auf der Saha-Boltzmann-Gleichung und auf den Konzentrationen der Arten, die individuiert wurden, berechnet wird.

6. Verfahren nach Anspruch 5, **dadurch gekennzeichnet, dass** der iterative Algorithmus folgende Schritte umfasst :

a) Festlegen eines Ausgangswerts für die Elektronendichte (N_e),

b) Berechnen der Konzentration der anderen Arten durch die Saha-Boltzmann-Gleichung,

c) Normalisieren jeder Konzentration in Bezug auf die Summe aller Konzentrationen, um den Verhältnisfaktor (F) zu beseitigen,

d) Berechnen der Elektronendichte (N_e) als die Summe der Konzentrationen (N_i) der ionisierten Arten,

e) Wiedereinbringen des Werts der Elektronendichte (N_e) in die Berechnung an Punkt b) und ein Wiederholen des Ablaufs, bis der Wert der Elektronendichte (N_e) konvergiert.

7. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** das Verfahren umfasst:

a) Individuierung der Spektrallinien;

b) Messung der Wellenlänge an einer mittleren Linie;

c) Messung des Linienintegrals.

8. Verfahren nach Anspruch 1 oder 7, **dadurch gekennzeichnet, dass** das Verfahren eine Identifizierung der Art durch Übereinstimmung zwischen der Wellenlängenmessung an der mittleren Linie und einer passenden Datenbank gemäß dem Höchstwahrscheinlichkeitskriterium umfasst.

9. Verfahren nach Anspruch 1, **gekennzeichnet durch** seine Anwendung für die Beschreibung von Metalllegierungen.

10. Verfahren nach Anspruch 1, **gekennzeichnet durch** seine Anwendung zur Beobachtung von Spurenelementen in der Atmosphäre.

11. Verfahren nach Anspruch 1, **gekennzeichnet durch** seine Anwendung zur Analyse von Böden vor Ort oder im Labor.

12. Verfahren nach Anspruch 1, **gekennzeichnet durch** seine Anwendung zur Analyse von Kulturerbe.

13. Verfahren nach Anspruch 1, **gekennzeichnet durch** seine Anwendung zur Atomemissionsspektroskopie.

14. System zur quantitativen Analyse von atomaren Bestandteilen von Materialien, die eine Vielzahl von Elementen enthalten, durch LIBS Spektroskopiemessungen, umfassend:

a) eine Laserstrahlungsquelle (1);

b) optische Mittel (2, 3) zum Richten der Laserquellenstrahlung zum Material;

c) ein optisches System (7) zum Empfangen der Strahlung, die durch das Plasma, das durch das Material erzeugt wurde, abgegeben wird;

d) ein System (9) zur Analyse des optischen Signals;

e) einen Computer (11), beinhaltend:

Mittel zum Messen der Stärke der Spektrallinien, die durch jedes Element abgegeben werden;

Mittel zum Erhalten der Plasmaelektronentemperatur (T) von zumindest einer Art der abgegebenen Strahlung;

dadurch gekennzeichnet, dass der Computer ferner beinhaltet:

Mittel zum Bestimmen der um einen Verhältnisfaktor (F) multiplizierten Konzentration (N_a) aller Arten;

Mittel zum Berechnen der Konzentration jedes Elements als Summe der entsprechenden Artenkonzentrationen;

Mittel zum Normalisieren jeder Konzentration in Bezug auf die Summe aller Konzentrationen, um den Verhältnisfaktor (F) zu beseitigen.

Revendications

1. Procédé de mesure quantitative de la concentration de composants atomiques de matériaux solides, liquides ou gazeux, comprenant :

   a) analyse spectrale du rayonnement, émis par un échantillon comprenant une pluralité d'éléments excités et ionisés de telle manière à générer un plasma ;
   b) analyse qualitative du rayonnement émis ;
   c) analyse quantitative sans étalonnage du rayonnement émis, ladite analyse quantitative comprenant les opérations consistant à :
   d) mesurer l'intensité des raies spectrales émises par chaque élément ;
   e) obtenir la température de plasma (T) d'au moins une espèce du rayonnement émis ;
   caractérisé par les opérations consistant à :
   f) déterminer la concentration (N_a) de toutes les espèces multipliée par un facteur de proportion (F) ;
   g) calculer la concentration de chaque élément comme étant la somme des concentrations des espèces correspondantes ;
   h) normaliser chaque concentration par rapport à la somme de toutes les concentrations, afin d'éliminer ledit facteur de proportion (F).

2. Procédé selon la revendication 1, **caractérisé en ce que** ladite température (T) est déterminée en effectuant une moyenne entre les mesures de plus d'une espèce.

3. Procédé selon la revendication 1, **caractérisé en ce qu'**il comprend en outre l'étape consistant à déterminer la valeur de la densité électronique (N_e).

4. Procédé selon la revendication 3, **caractérisé en ce que** si la concentration (FN_a) pour seulement l'une des espèces est disponible la concentration des autres espèces est calculée au moyen de l'équation de Saha-Boltzmann.

5. Procédé selon la revendication 1, **caractérisé en ce que** si la concentration (FN_a) pour seulement l'une des espèces est disponible et que la valeur de la densité électronique (N_e) n'est pas connue, la concentration des autres espèces est calculée en tant que valeur de convergence d'un algorithme itératif basé sur l'équation de Saha-Boltzmann et sur les concentrations des espèces qui ont été individualisées.

6. Procédé selon la revendication 5, **caractérisé en ce que** ledit algorithme itératif comprend l'étape consistant à :

   a) établir une valeur de départ pour la densité électronique (N_e),
   b) calculer la concentration des autres espèces au moyen de l'équation de Saha-Boltzmann,
   c) normaliser chaque concentration par rapport à la somme de toutes les concentrations, afin d'éliminer ledit facteur de proportion (F),
   d) calculer la densité électronique (N_e) en tant que somme des concentrations (N_i) des espèces ionisées,
   e) réintroduire la valeur de la densité électronique (N_e) dans le calcul du point b), et répéter le cycle jusqu'à ce que la valeur de la densité électronique (N_e) converge.

7. Procédé selon la revendication 1, **caractérisé en ce que** ledit procédé comprend :

a) individualisation des raies spectrales ;
b) mesure de la longueur d'onde au milieu d'une raie ;
c) mesure de l'intégrale de raie.

8. Procédé selon la revendication 1 ou 7, **caractérisé en ce que** ledit procédé comprend l'identification des espèces par la correspondance entre la mesure de longueur d'onde au milieu d'une raie et une base de données appropriée, selon le critère de probabilité maximale.

9. Procédé selon la revendication 1, **caractérisé par** son application pour la caractérisation d'alliages métalliques.

10. Procédé selon la revendication 1, **caractérisé par** son application pour surveiller des radioéléments indicateurs dans l'atmosphère.

11. Procédé selon la revendication 1, **caractérisé par** son application pour l'analyse de sols in situ ou en laboratoire.

12. Procédé selon la revendication 1, **caractérisé par** son application pour l'analyse de l'héritage culturel.

13. Procédé selon la revendication 1, **caractérisé par** son application pour la spectroscopie par émission atomique.

14. Système pour l'analyse quantitative de composants atomiques de matériaux comprenant une pluralité d'éléments par des mesures de spectroscopie LIBS comprenant :

a) une source de rayonnement laser (1) ;
b) un moyen optique (2, 3) pour diriger le rayonnement de source laser vers le matériau ;
c) un système optique (7) pour recevoir le rayonnement émis par le plasma généré par le matériau ;
d) un système d'analyse (9) de signaux optiques ;
e) un ordinateur (11) comportant :

un moyen pour mesurer l'intensité des raies spectrales émises par chaque élément ;
un moyen pour obtenir la température électronique de plasma (T) d'au moins une espèce du rayonnement émis ;

caractérisé en ce que ledit ordinateur comprend en outre

un moyen pour déterminer la concentration (N_a) de toutes les espèces multipliée par un facteur de proportion (F) ;
un moyen pour calculer la concentration de chaque élément comme étant la somme des concentrations des espèces correspondantes ;
un moyen pour normaliser chaque concentration par rapport à la somme de toutes les concentrations, afin d'éliminer ledit facteur de proportion (F).

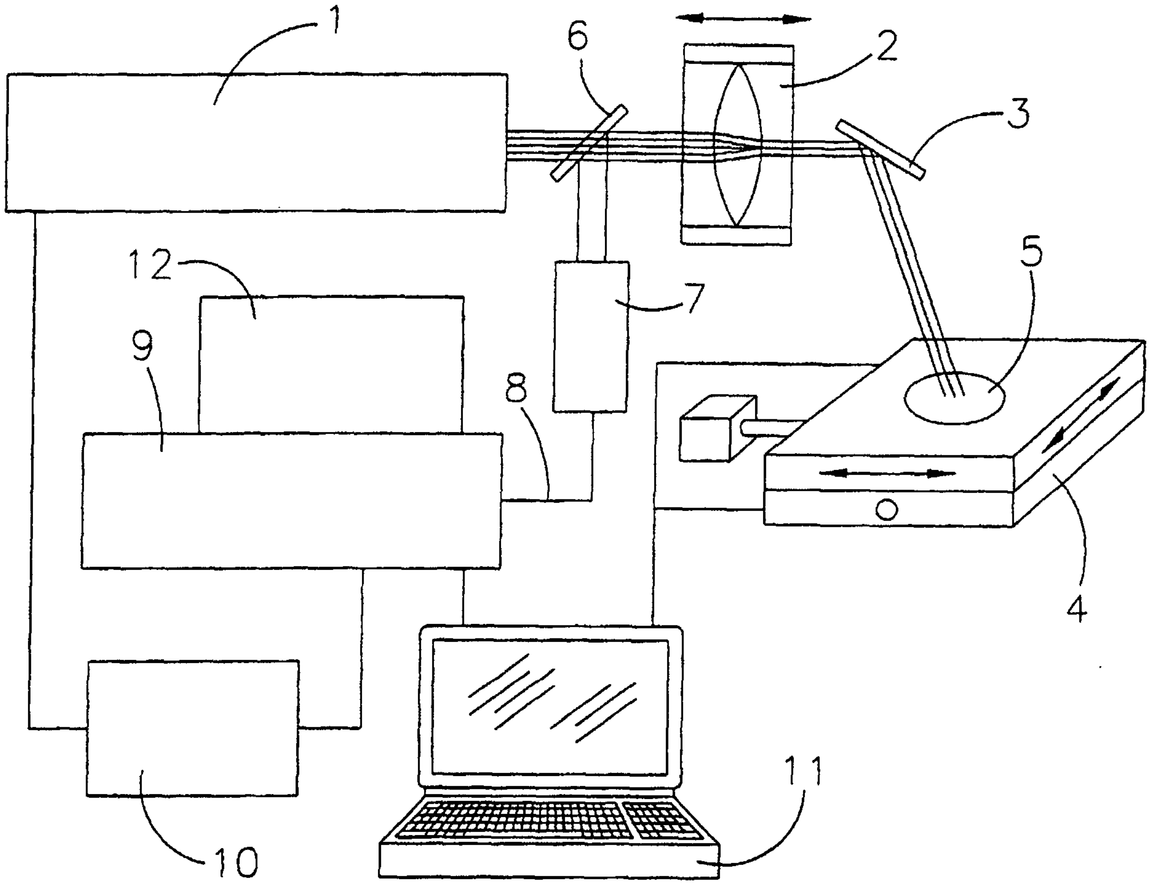

FIG. 1

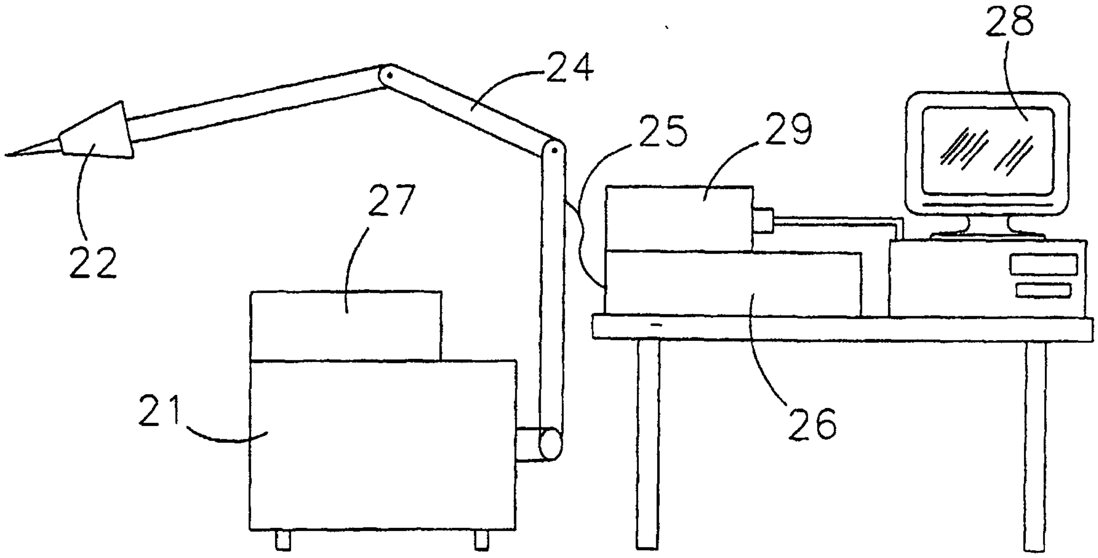

FIG. 2

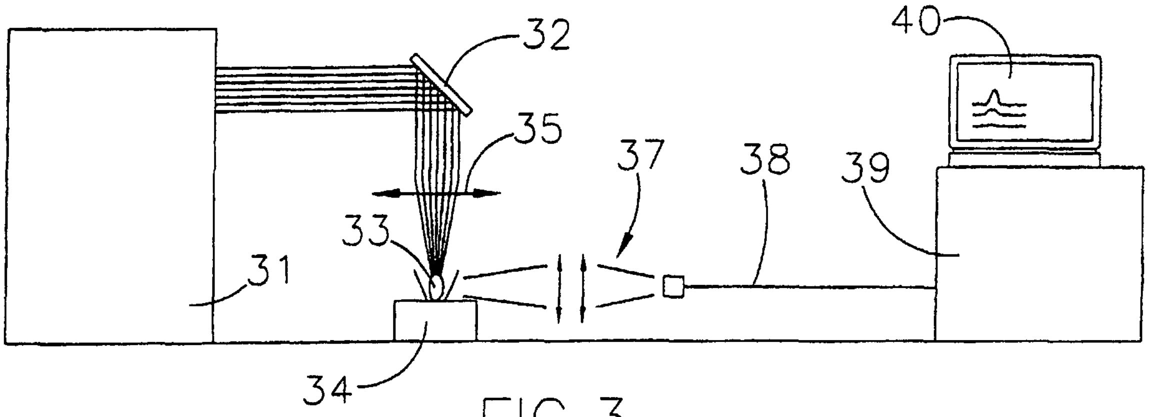

FIG.3

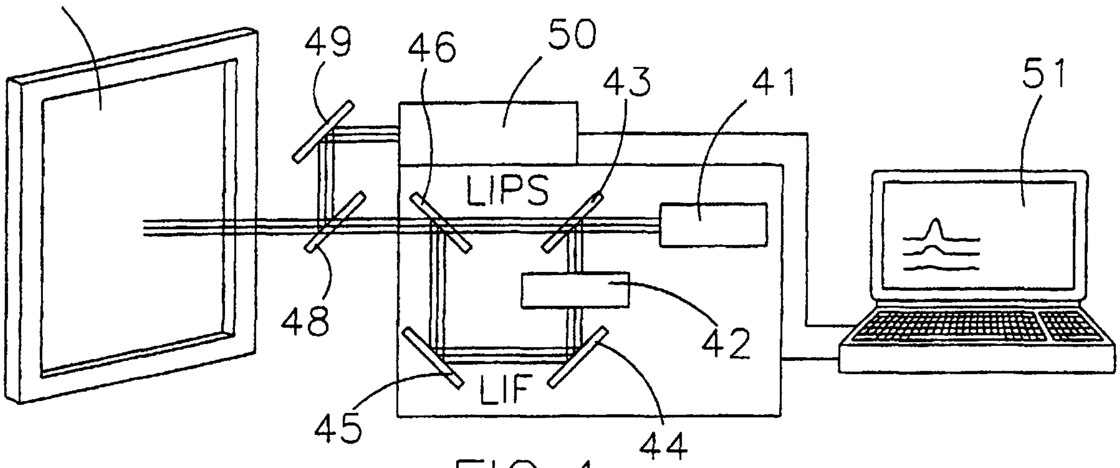

FIG.4

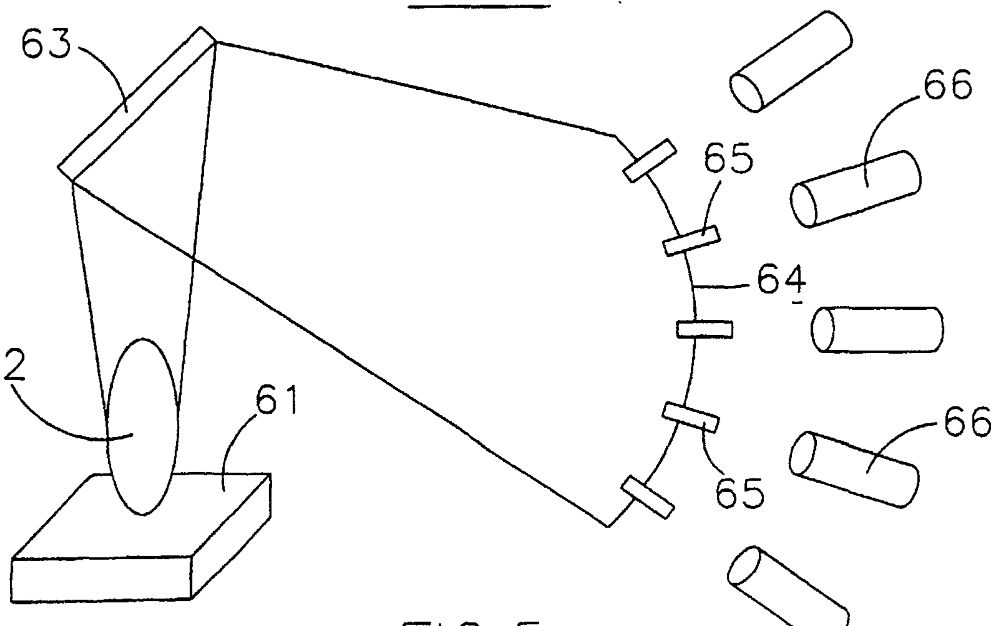

FIG.5

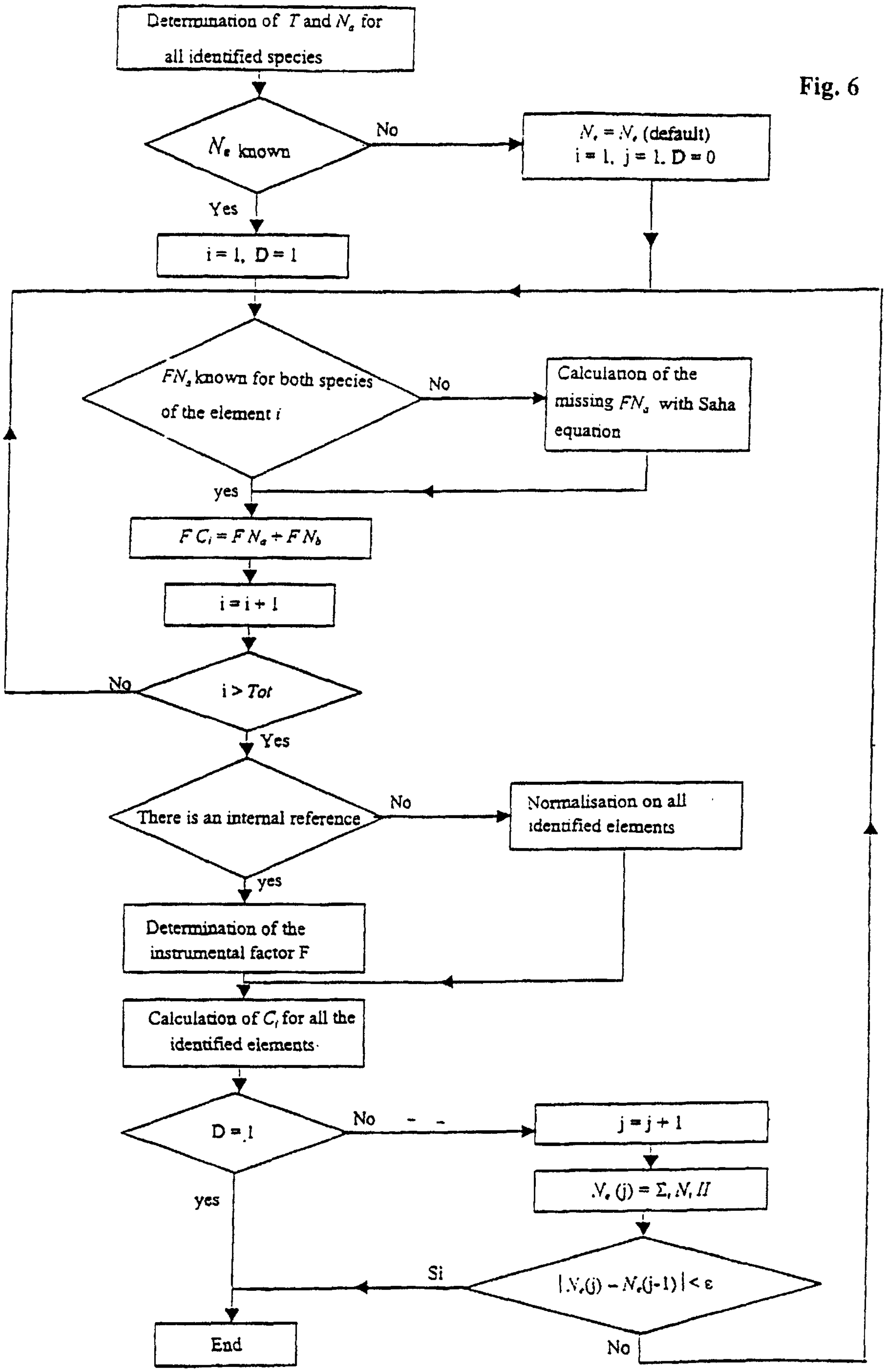
Determination of T and N_a for all identified species
N_e known
No
$N_e = N_e$ (default)
i = 1, j = 1, D = 0
Yes
i = 1, D = 1
FN_a known for both species of the element i
No
Calculation of the missing FN_a with Saha equation
yes
$F C_i = F N_a + F N_b$
i = i + 1
No
i > Tot
Yes
There is an internal reference
No
Normalisation on all identified elements
yes
Determination of the instrumental factor F
Calculation of C_i for all the identified elements
D = 1
No
j = j + 1
$N_e(j) = \Sigma_i N_i II$
yes
Si
$|N_e(j) - N_e(j-1)| < \varepsilon$
End
No

Fig. 6

Determination of the working regime:

a) energy of the laser pulse and repetition rate;
b) focusing and receiving optics;
c) delay and duration of the acquisition gate.
d) spectrometer set up

Spectra Acquisition at fixed working spot

Spectra Analysis:

a) individuation of the lines;
b) measurement of the wavelength at mid line;
c) measurement of the line integral.

Qualitative analysis:

identification of the species through correspondence between the measurement at mid line and proper database, according to the maximum probability criterion.

Quantitative analysis:

a) calculation of the temperature T on at least one species;
b) calculation of the partition function of each species;
c) calculation of the concentration of the species times the experimental factor F;
d) calculation of the concentration of the species that have not been individuated by Saha equation;
e) calculation of the concentration of the elements as a sum of the concentrations of the species;
f) measurement of the concentration of the elements through elimination of the F factor by means of normalisation or internal reference.

Fig. 7