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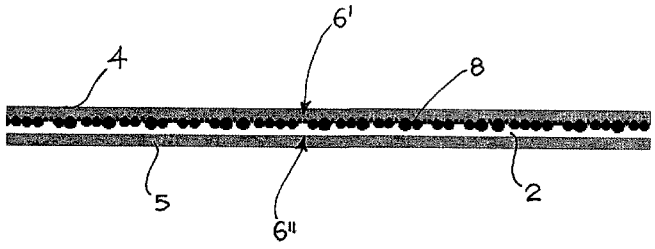

Fig. 1b

(57) Abstract: The present invention relates to a method for the analysis of a sample by means of radiation, for example using X-ray techniques. The method comprises a first step of providing a substrate, for example a filter, having an substantially flat shape and comprising a first and a second main surface. The method further comprises a step of depositing an analyte on the substrate, for example a particulate, and a step of coating at least a first area comprising the analyte of at least one of the main surfaces with a layer or film, to obtain a sample at least partially coated. Such film is at least partially permeable to the radiation used in the analysis. Furthermore the method comprises a step of analysing the first coated area of the sample by means of the radiation passing through the film.

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"Method for the analysis of samples and sample"

DESCRIPTION

[0001] . The present invention regards a method for the analysis of samples, for example using X-rays, and a sample .

[0002] . Analytical methods are known of in the art, for example for environmental samples, wherein a collecting filter, on the surface of which are dispersed mainly solid compounds to be analysed, are dissolved or, as it is use to say in the language of the field, "digested" in a solvent. Subsequently, the resulting solution is analysed using various techniques, for example by means of inductively coupled plasma spectrometry combined with mass spectrometry (ICP-MS) or atomic absorption spectrometry (AAS) .

[0003] . Alternatively, it is known to analyze the filters as such, i.e. inserting them directly inside the analysis instrument .

[0004] . However, the methods of the known technique suffer a plurality of drawbacks.

[0005] . Specifically, the digestion of the filters, as well as being a destructive technique which is usually extremely long to perform, entails the introduction of possible errors in the analysis.

[0006] . Furthermore, the analysis of the filter as such

usually produces contamination of both the instrument and the sample, with negative effects on subsequent analyses.

[0007] . The method of the present invention therefore sets out to resolve the drawbacks of the known technique and, specifically, those mentioned before.

[0008] . Such aim is achieved by means of a method according to claim 1 and by means of a sample according to claim 18. The dependent claims show embodiment variations .

[0009] . The object of the present invention will now be described in detail, with the help of the attached figures, wherein:

[0010] . - figures Ia and Ib show a diagram of two transversal cross-sections of a sample, subjected to the method of the present invention, according to possible embodiments ;

[0011] . - figure 2 shows two TXRF superimposed spectrums of the same sample using the method of the present invention (darker area) and the method of introducing the sample as such (lighter area) ;

[0012] -.-_- -figure 3 shows the TXRF spectrum _relative to the sample standard NIST 2783-1752, obtained using the method of the present invention and object of example 1 ;

[0013] . - figure 4 shows the TXRF spectrum, obtained using the present method, relative to an analysis filter,

comprising atmospheric particulate and gallium, the latter present in the role of internal standard.

[0014] . A method according to the invention for the analysis of samples, by means of radiation, for example using X-ray techniques, comprises a first step of providing_a substrate or collecting medium 2, such as a filter, having an substantially flat shape and comprising a first 6' and a second 6" main surface.

[0015] . In two subsequent steps of the method, a material to be analysed or analyte 3, such as a particulate, is deposited on the substrate 2, and at least a first area comprising the analyte 3, of at least one of the main surfaces 6', 6", is coated with a layer or film 4, 5 to produce a sample 1, 1' at least partially coated. Such film 4, 5 is at least partially permeable to the radiation used in the analysis.

[0016] . Preferably, the film 4, 5 is completely permeable or transparent to the radiation used.

[0017] . In other words, the first area coated by the film 4, 5 substantially constitutes an analysis area, whicltrroccupies at least a partial surface of-r-~the substrate 2 smaller than the total surface of the same.

[0018] . Preferably, the first area corresponds to the _total surface of the sample, that is, to the extension of the first 6' and/or second 6" main surface.

[0019] - With reference to the transversal cross-section of figures Ia, after the step of coating, the sample 1 has a structure comprising a substrate or collecting medium 2, such as for example a filter, the analyte 3 deposited at least partially on the surface of the substrate 2, for example a particulate, and the film 4, 5.

[0020] . Preferably, the substrate 2 is permeable to gases, for example to air.

[0021] . Even more preferably, the substrate 2 comprises at least one area in fibrous or spongy material, suitable for allowing the free passage of a flow of gas through the substrate 2, and for retaining in the substrate 2 a particulate transported by such flow.

[0022] . In other words, the substrate 2 identifies channels or pores within itself, suitable for allowing the free passage of the flow of gas through the substrate 2, and for retaining in the substrate 2 the particulate transported by such flow.

[0023] . According to one possible embodiment, the zdxameter of such pores is between 0.05 and 10 micrometers and, preferably, between 0.1 and 0.5 micrometers.

[0024]. According to an embodiment, the substrate 2 is made from a material comprising poly-tetrafluoroethylene (PTFE), polycarbonate, polyamide, nylon, (methyl-)

cellulose.

[0025]^— According to one advantageous embodiment variation, the film 4, 5 adheres to the surface of the substrate 2 at least in the first area.

[0026] . In other words, the film 4, 5 is able to reduce _at least partially the imperfections- of the main surfaces 6', 6", in order to provide a substantially planar and more homogeneous analysis area, suitable for being evenly hit by the radiation used in the analysis, as will be explained below.

[0027] . According to an embodiment variation, the film 4, 5 is suitable for modifying its aggregation state before and after the step of coating the sample.

[0028] . In other words, the coating of the sample with the film 4, 5 may be performed in hot or cold conditions, i.e. at different temperatures, using mechanical, chemical or chemical-physical means. Obviously the choice of method used depends on the nature of the sample to be analysed and/or the type of analysis to be performed.

[0029] . In a further variation, after the step of coating 7=ethe-film 4, 5 is substantially=-in^solid form, in order to constitute a protective superficial layer, for example permanent , for the substrate 2 and the analyte 3.

[0030] ._ Preferably, the film 4, 5 is mainly made from an organic solid, such as polymer.

[0031] . Even more preferably, the film 4, 5 is free of metals which might make complex the results analysis.

[0032]. According to one embodiment, the film 4, 5 comprises a thermosetting or thermoplastic polymer, such as an epoxy resin, polyurethane, polypropylene, polyethylene, polycarbonate, polystyrene,- polyamide, PVC, nylon, or mixtures thereof.

[0033]. According to a further variation, the film 4, 5 comprises thin layers of inorganic materials, such as Al_2O_3, TiO_2 and/or ZnO.

[0034] . According to yet a further variation, the film 4, 5 is made from a combination of the different mentioned organic/inorganic layers.

[0035] . According to one embodiment, the thickness of the film 4, 5 is between 10 nanometres and 2 millimetres and, preferably, between 50 nanometres and 1 millimetre.

[0036] . According to a preferred embodiment, the step of coating comprises the step of coating at least a first area of both main surfaces 6', 6".

[0037]. In other words, the substrate 2 is coated at least partially both on the main surface 6', facing the radiation source, and on the main surface 6" opposite to such source .

[0038]. With reference to the transversal cross-section of figure Ib, after the coating step, the sample 1'

presents a structure comprising, in the direction - traversed by the radiation, the film 4, the analyte 3, the substrate 2 and the film 5.

[0039]. According to this embodiment, the substrate 2 and the analyte 3 are embedded between the two films 4, 5.

[0040]. According to an advantageous embodiment, the method further comprises a step of extending the film 4, 5 beyond the main surfaces 6', 6" to create an external portion.

[0041]. In other words, according to this embodiment, the sample 1, 1' comprises an external portion comprising the film 4, 5, extending externally to the main surfaces 6', 6".

[0042]. In still other words, the film 4, 5 coats the main surfaces 6', 6" of the substrate 2 and extends externally beyond its peripheral limit.

[0043]. According to different embodiments, such external portion is suitable for being gripped and/or cut by an operator.

[0044]. In fact, according to a preferred variation, the method further comprises a step of shaping the external portion, for example by cutting it, to the seating of an analysis instrument.

[0045]. In other words, the presence of a portion of

film 4, 5 external to the area occupied by the substrate 2 makes it possible to shape its dimensions, in order to adapt them to the shape of the sample holder of any analytical instrument .

[0046] . According to a further preferred variation, the method further comprises a step of grasping the external portion in order to handle the sample 1, 1'.

[0047]. In other words, the portion of film 4, 5 exceeding the external perimeter of the substrate constitutes a gripping portion for the operator, suitable for being held or gripped.

[0048] . In other words, an operator may handle the sample in a peripheral area, external to the surface of the same, which will not be subjected to the analysis, in order to prevent possible contamination of the sample.

[0049] . Furthermore the method comprises a step of analysing the first coated area of the sample 1, 1' by means of the radiation passing through the film 4, 5.

[0050] . In other words, the presence of the film 4, 5 between the source of radiation and one of the surfaces of the substrate 2 comprising the analyte 3 to be analysed makes it possible to improve the quality of the experimental spectrum, such as the intensity, the separation and/or the resolution of the peaks. To such purpose refer to figure 2, where the spectrum with the

darker area shows the signal obtained using the method of the present invention, while the lighter area shows the signal obtained using the method of introduction of the sample as such, without the protective coating of the film 4, 5. Such spectrum was obtained from the analysis of a mixture comprising a calcium-sulphate salt ($CaSO_4$).

[0051]. In still other words, the film 4, 5 provides a more homogenous and substantially planar analysis area, in order to increase the achievable analysis sensitivity. Such sensitivity can in fact be increased till parts per billion (ppb).

[0052]. In yet other words again, the presence of an analysis area, having a surface facing the source of radiation which is substantially planar, produces a net improvement in the quality of the experimental spectrum and in the reproducibility of the analysis.

[0053]. Preferably, during the passage of the radiation through the film 4, 5, such film 4, 5 remains substantially intact and unaltered.

[0054]. In other words, the method is not destructive therewith regard to the sample to be analysed, nor with regard to the film 4, 5.

[0055]. In other words again, the film 4, 5 is permeable or transparent to the incident radiation, so as not to undergo alterations, such as degradation or vaporisation

of material, deriving from the energy of such radiation.

[0056] According to one advantageous embodiment, the coating step comprises a hot or cold lamination.

[0057] According to a further embodiment, the step of coating comprises a plasticization step, for example in hot or cold conditions.

[0058] According to such embodiments, as already hinted above, the step of coating comprises a step of coating with a film 4, 5 comprising a thermosetting or thermoplastic polymer, such as for example an epoxy resin, polyurethane, polypropylene, polyethylene, polycarbonate, polystyrene, polyamide, PVC, nylon, or mixtures thereof, or with a film 4, 5 comprising thin layers of inorganic materials, such as Al_2O_3, TiO_2 and/or ZnO.

[0059] According to a further variant, the step of analyzing comprises a qualitative and/or quantitative analysis of the sample.

[0060] In other words, according to this embodiment, it is possible to establish the chemical composition, for example, byzmeans of TXRF, and the phases, for example by diffraction, of the analytes 3 present on the substrate to be analysed.

[0061] In other words again, from the qualitative analysis provided by a specific instrument, it is

possible to estimate also the quantities of the elements present, for example of metals and/or metal oxides.

[0062] . In a possible embodiment, such quantitative derivation is performed by means of the analysis of standard samples, for example supplied by the "National Institute of Standards and Technology"-- (NIST) .

[0063] . According to a further variant, the step of providing the substrate 2 comprises the steps of providing at least one rigid support for the substrate 2, and joining the support and the substrate 2 to obtain a supported substrate.

[0064] . In other words if, the substrate 2 has, for example, an insufficiently manageable physical form and if the rigidity of the film 4, 5 is insufficient to improve such condition, the substrate may be initially placed on a further support and then the whole may be subjected to the subsequent step of coating.

[0065] . According to a further embodiment variation the support comprises reference information of the sample 1, 1' to be analysed, for example a reference abbreviation, a barcode or a RFID- transponder (Radio- Frequency Identification) , to univocally identify such sample.

[0066] . This way, the risk of mistaking the identity of the samples 1, 1' analysed is considerably reduced.

[0067] . According to one embodiment, the step of coating

further comprises a step of coating the supported substrate, in order to subject it to analysis together with the support.

[0068] . According to a preferred variation, the method further comprises the steps of providing at least one standard reference substance, and depositing the standard reference substance on a second area overlapping at least partially the first area.

[0069] . According to one embodiment variation, the standard reference substance is deposited on a second area on the surface of the film 4, 5 suitable for contacting the substrate 2, or on a second area disposed on the surface of the substrate 2 destined to contact the film 4, 5.

[0070] . According to a further variation, the standard reference substance is deposited on a second area disposed on the surface of the film 4, 5 opposite to that destined to be joined to the substrate 2.

[0071] . According to yet a further variation, the standard reference substance occupies a second area internal-to the thickness of the film 4, 5.

[0072] . In other words, according to this embodiment variation, the sample 1, 1' comprises a standard substance not contained in the sample to be analysed and functioning as an internal standard.

[0073] . In still other words, the standard substance which, during the analysis, is expected to behave like the analyte 3, is added in a known quantity. This way, the quantity of the standard substance being known, but that of the analyte 3 being unknown, it is possible to evaluate the concentration of the analyte 3 in relation to the standard.

[0074] . To such purpose, refer for example to the spectrum of figure 4, where a known quantity of a standard comprising mainly gallium was added to a sample of atmospheric particulate to enable the quantitative determination of the other elements in relation to the known quantity of the standard.

[0075] . Preferably, the analysis step comprises a fluorescence of X-rays in total reflection (TXRF) analysis, for which the present method proves particularly suitable.

[0076] . According to a further variation, the step of analyzing comprises an analysis by means of diffraction of X-rays or of neutrons .

[0077] . According to one advantageous variation, the method further comprises a step of archiving the sample 1, 1' at least partially coated.

[0078] . In other words, being the substrate 2 and the analyte 3 at least partially protected by the film 4, 5,

it is possible to create an archive of samples previously analysed, in order to subjecting them to further analysis, even after the passage of time.

[0079] . In other words again, being the samples 1, 1' protected by the film 4, 5, they are not subject to deterioration as a result of the effects of atmospheric agents, nor to the accidental loss of the analyte 3.

[0080] . Moreover, on the contrary, samples which would otherwise be "at risk" can be transported and/or handled, especially biological samples posing a health risk to the operators .

[0081] . The present invention also relates to a sample 1, 1' for the analysis of samples by radiation, for example using X-ray techniques, comprising a substrate or collecting medium 2, such as a filter, having an substantially flat shape and comprising a first 6' and a second main surface 6", and a material to be analysed or analyte 3, such as a particulate, deposited on the substrate 2.

[0082]. The sample 1, 1', for example, environmental or biological, further comprises at least one layer or film 4, 5, at least partially permeable to the radiation used in the analysis, which coats at least a first area of at least one of the main surfaces 6', 6" comprising the analyte 3.

[0083] . According to one embodiment, the sample 1, 1' comprises in addition at least one rigid support joined to the substrate 2 to support it .

[0084] . EXAMPLE 1

[0085] . Verification of the reliability of quantitative assessment using the present method, in relation to a standard of known composition.

[0086] . In this example the known percentage compositions taken from the technical specifications of the standard NIST 2783-1752 were compared with the average percentage values obtained experimentally from TXRF analysis. The spectrum corresponding to the present example is shown in figure 3 .

[0087] . The results obtained are summarised in the following table:

	Average experimental values	Certified values for standard NIST 2783-1752	
Element	Percentage in weight	Percentage in weight	Percentage deviation
Ti	4.0	4.8	± 16
Cr	0.38	0.43	± 19
Mn	0.89	1.04	± 4
Fe	85.7	86.2	± 6
Ni	0.19	0.22	± 18
Cu	1.4	1.3	± 10
Zn	7.4	5.8	± 7
Rb	0.07	0.08	± 23

[0088] . As can be seen, almost all the values measured experimentally are comparable to the known percentages of

the standard's technical specifications.

[0089] . Innovatively, the method of the present invention, makes it possible to increase the recognition's sensitivity of the chemical elements within the sample, compared to the known state-of-the-art methods.

[0090] . Advantageously, such increased sensitivity occurs without the need to acquire further analytic instrumentation, such as a more sensitive detector, because this increase occurs presumably as a result of a homogeneous and substantially planar analysis area.

[0091] . Advantageously, the method of the present invention permits direct analysis of the samples. This way the use of reagents is not required, limiting both the environmental impact of the technique, and the introduction of external contaminants into the analysis environment .

[0092] . Advantageously, in the method of the present invention no insoluble portion of .the sample being analysed is lost, enabling precise and accurate analysis of the entire sample.

[0093] . Advantageously, the method of the present invention prevents contamination of the analytic instrument after each analysis, and the resulting negative effects on subsequent analyses.

[0094] . Advantageously, the method of the present invention makes it possible to drastically reduce the time required for each analysis, from tens of hours to tens of minutes .

[0095] . Advantageously, the method of the present invention makes it possible to conduct, in a reproducible manner and with a single analytic assay, both a qualitative and quantitative assessment of the elements and phases present in the sample.

[0096] . Advantageously, the voluntary inclusion of compounds, for example metallic, inside the film 4, 5 makes it possible to create reference standards for an immediate also quantitative analysis.

[0097] . Advantageously, the presence of a solid manageable by anyone makes> it possible to adapt the dimensions of the sample to those of any sample holder very easily, eliminating the problem of reduced or even inadequate analysis areas.

[0098] . Advantageously, the method of the present invention makes it possible to conserve the samples, without their deterioration with the passage of time. This way, it is furthermore possible to create an archive of samples in order to subjecting them to further testing, if necessary, even at a later date.

[0099] . Furthermore, advantageously, the method of the

present invention makes samples otherwise "at risk", especially for the operators handling them, transportable.

[00100]. Advantageously, the samples subjected to the present method can be suitably supported so that the sample information is permanently joined to the relative support, without the risk of accidental loss or mismatching of the two.

[00101]. Advantageously, the simplicity of coating the samples makes it possible to use both samples and supports of non-equivalent thicknesses, non-standardised or non-uniform, without the sensitivity or reliability of the analysis being affected.

[00102]. Advantageously, the method of the present invention permits a versatile application in various analytical techniques, ranging from environmental analysis to the analysis of biological samples.

[00103]. Advantageously, the method of the present invention makes it possible to make a direct comparison between samples, so that the differences are evident *prima facie*, without the need to re-processing the data.

[00104]. A person skilled in the art may make modifications to the embodiments of the method described above so as to satisfy contingent requirements while remaining within the sphere of protection of the

following claims.

[00105] . Each of the features described as belonging to a possible embodiment may be performed independently form the other embodiments described.

CLAIMS

1. Method for the analysis of a sample (1, 1') by means of radiation, for example using X-ray techniques, comprising the steps of:

- providing a substrate or collecting medium (2), such as a filter, having an substantially flat shape and comprising a first (6') and a second (6") main surface;
- depositing a material to be analysed or analyte (3), such as a particulate, on the substrate (2);
- coating at least a first area comprising the analyte (3) of at least one of the main surfaces (6', 6") with a layer or film (4, 5) at least partially permeable to the radiation used in the analysis, to obtain a sample (1, 1') at least partially coated;
- analysing the first coated area of the sample (1, 1') by means of the radiation passing through the film (4, 5).

2. Method according to claim 1, wherein during the passage of the radiation through the film (4, 5), said film (4, 5) remains substantially intact and unaltered.

3. Method according to claim 1 or 2, wherein the step of coating comprises the step of coating at least a first area of both main surfaces (6', 6").

4. Method according to any of the previous claims, further comprising a step of extending the film (4, 5)

beyond the main surfaces (6', 6") creating an external portion.

5. Method according to claim 4, further comprising a step of shaping the external portion, for example by cutting it, to the seating of an analysis instrument.

6. Method according to claim 4 or 5, further comprising a step of gripping the external portion in order to handle the sample (1, 1').

7. Method according to any of the previous claims, wherein the step of coating comprises a hot or cold lamination.

8. Method according to any of the previous claims, wherein the step of coating comprises a plasticization step.

9. Method according to claim 7 or 8, wherein the step of coating comprises a step of coating using a film (4, 5) comprising a thermosetting or thermoplastic polymer, such as an epoxy resin, polyurethane, polypropylene, polyethylene, polycarbonate, polystyrene, polyamide, PVC, nylon, or mixtures thereof.

10. Method according to any of the previous claims, wherein the step of coating comprises a step of coating using a film (4, 5) comprising thin layers of inorganic materials such as Al_2O_3, TiO_2 and/or ZnO.

11. Method according to any of the previous claims,

wherein _the__ step of analyzing comprises a qualitative and/or quantitative analysis of the sample.

12. Method according to any of the previous claims, further comprising the steps of:

- providing at least one standard reference substance; and

- depositing the standard reference substance on a second area overlapping at least partially the first area.

13. Method according to any of the previous claims, wherein the step of analyzing comprises a fluorescence of X-rays in total reflection (TXRF) analysis.

14. Method according to any of the previous claims, wherein the step of analyzing comprises an analysis by means of diffraction of X-rays or of neutrons.

15. Method according to any of the previous claims, wherein the step of providing the substrate (2) comprises the steps of:

- providing at least one rigid support for the substrate (2)_;

- joining the support and the substrate (2) to obtain a supported -substrate .

16. Method according to claim 13, wherein the step of coating further comprises a step of coating the supported substrate .

17. Method according to any of the previous claims,

further comprising a step of archiving the at least partially coated sample (1, 1')-

18. Sample (1, 1') for analysis by means of radiation, for example using X-ray techniques, comprising:

- a substrate or collecting medium (2), such as a filter, having an substantially flat shape and comprising a first (6') and a second (6") main surface;

- a material to be analysed or analyte (3), such as a particulate, deposited on the substrate (2);

- at least one layer or film (4, 5), at least partially permeable to the radiation used in the analysis, coating at least a first area comprising the analyte (3) of at least one of the main surfaces (6', 6").

19. Sample (1, 1') according to claim 18, wherein the substrate (2) is permeable to gases.

20. Sample (1, 1') according to claim 18 or 19, wherein the substrate (2) comprises at least one area in fibrous or spongy material, suitable for allowing the free passage of a flow of gas, such as air, through the substrate (2), and for retaining in the substrate (2) a particulate transported by such flow.

21. Sample (1, 1') according to any of the claims from 18 to 20, wherein the substrate (2) identifies channels or pores within itself, suitable for allowing the free passage of the flow of gas through the substrate (2), and

for retaining in the substrate (2) the particulate transported by such flow.

22. Sample (1, 1') according to claim 21, wherein the diameter of said pores is between 0.05 and 10 micrometers and, preferably, between 0.1 and 0.5 micrometers.

23. Sample (1, 1') according to any of the claims from 18 to 22, comprising an external portion comprising the film (4, 5), extending externally to the main surfaces (6', 6").

24. Sample (1, 1') according to claim 23, wherein the external portion is suitable for being gripped and/or cut.

25. Sample (1, 1') according to any of the claims from 18 to 24, wherein the substrate (2) is made from a material comprising poly-tetrafluoroethylene (PTFE), polycarbonate, polyamide, nylon, (methyl-) cellulose.

26. Sample (1, 1') according to any of the claims from 18 to 25, wherein the film (4, 5) adheres to the surface of the substrate (2) at least in the first area.

27. Sample (1, 1') according to any of the claims from 18 to 26, wherein the film (4, 5) comprises a thermosetting or thermoplastic polymer, such as an epoxy resin, polyurethane, polypropylene, polyethylene, polycarbonate, polystyrene, polyamide, PVC, nylon, or mixtures thereof.

28. Sample (1, 1') according to any of the claims from 18

to 27, wherein the film (4, 5) comprises thin layers of inorganic materials, such as Al_2O_3, TiO_2 and/or ZnO.

29. Sample (1, 1') according to any of the claims from 18 to 28, wherein the thickness of the film (4, 5) is between 10 nanometres and 2 millimetres and, preferably, between 50 nanometres and 1 millimetre.

30. Sample (1, 1') according to any of the claims from 18 to 29, further comprising at least one rigid support joined to the substrate (2) to support it.

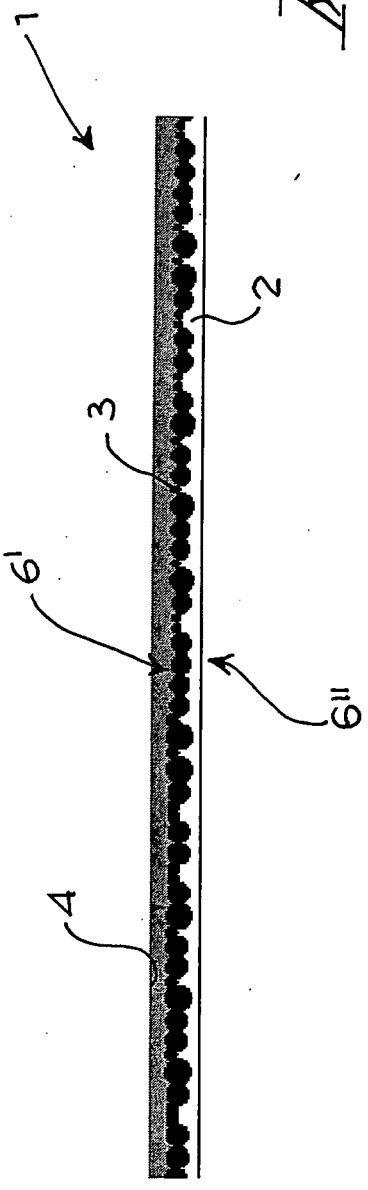

Fig. 1a

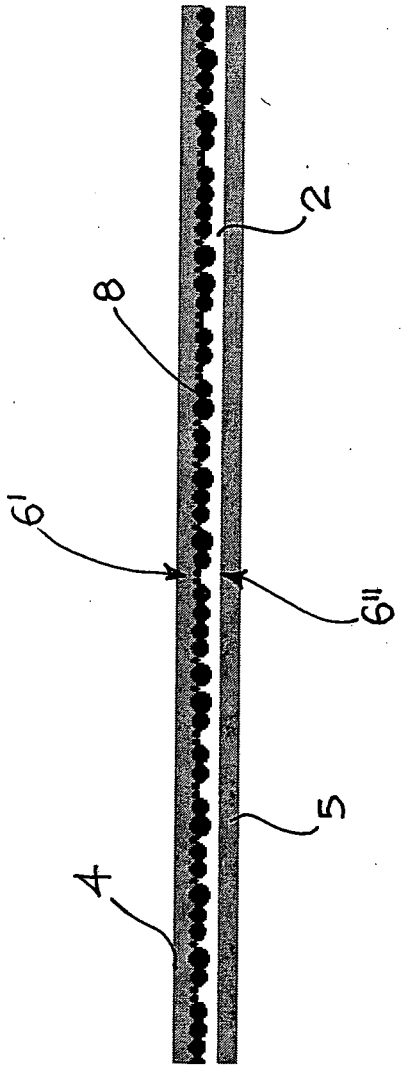

Fig. 1b

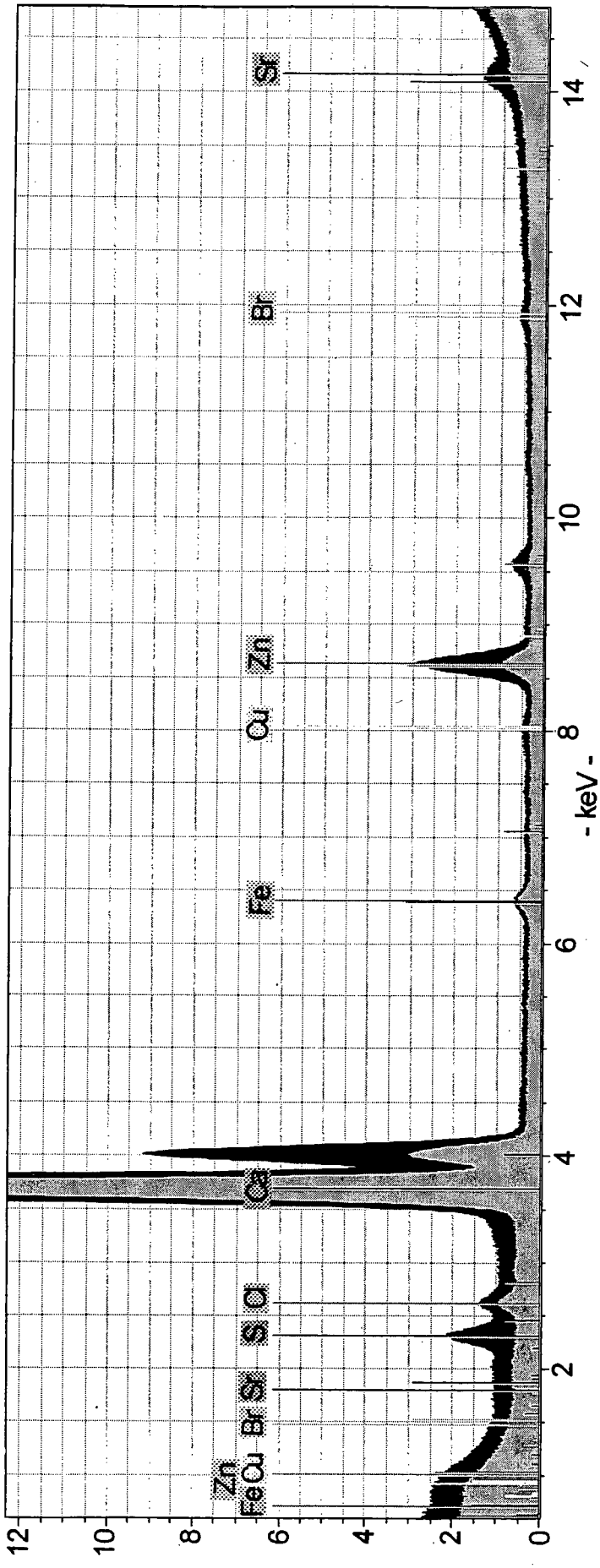

Fig.2

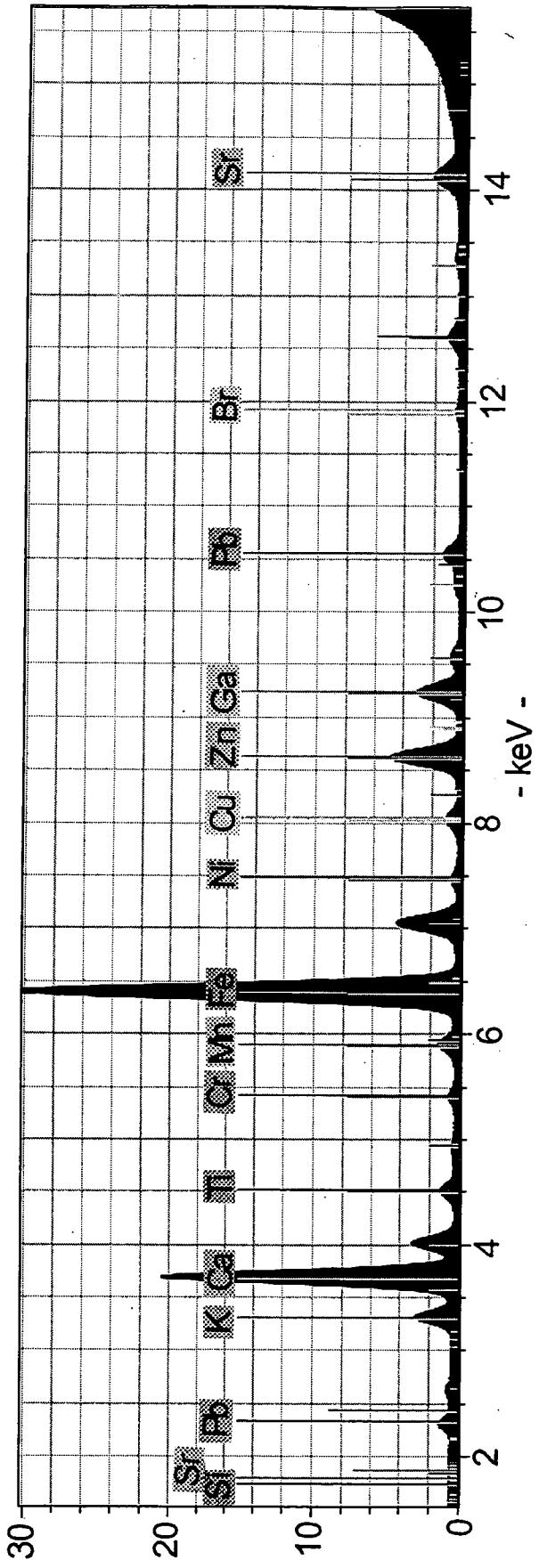
Sr
Br
Rb
Zn Ga
Cu
Ni
Cr Mn Fe
Ti
K Ca
Pb
Sr Sr
0
10
20
30
2
4
6
8
10
12
14
- keV -

Fig.3

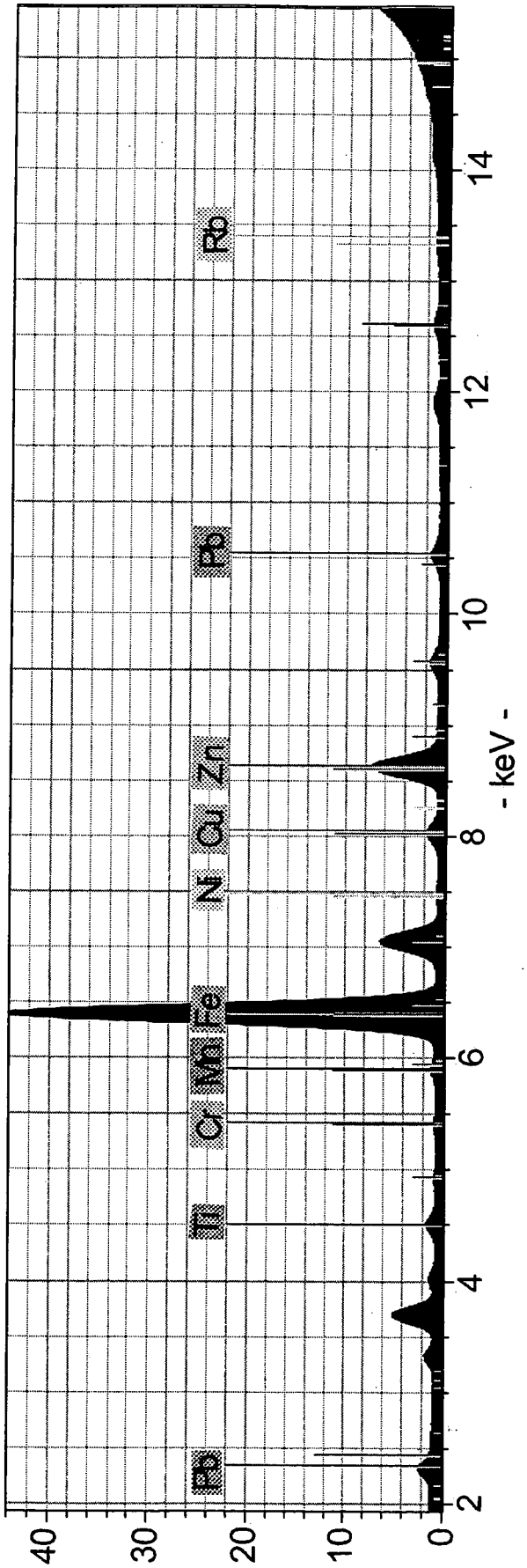

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2008/000458

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N1/36

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

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 575 691 A (POLLARD ALAN ET AL) 20 April 1971 (1971-04-20) column 1, line 15 - column 3, line 61	1-30
X	US 5 012 681 A (LENTZEN DONALD E [US]) 7 May 1991 (1991-05-07) abstract column 1, line 10 - column 3, line 30; figure 1	1-30
X	US 4 530 250 A (GAY DON D [US] ET AL) 23 July 1985 (1985-07-23) abstract column 4, line 39 - line 44	1,18

D Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"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	Date of mailing of the international search report
17 April 2009	27/04/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	van Lith, Joris

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IT2008/000458

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3575691 A	20-04-1971	BE 695492 A	14-08-1967
		CH 526325 A	15-08-1972
		DE 1598938 Al	18-03-1971
		FR 1514624 A	23-02-1968
		GB 1187202 A	08-04-1970
		SE 333071 B	01-03-1971
US 5012681 A	07-05-1991	NONE	
US 4530250 A	23-07-1985	CA 1229504 Al	24-11-1987
		DE 3512854 Al	17-10-1985
		FR 2563006 Al	18-10-1985
		GB 2157431 A	23-10-1985