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Method Article

Recovering and restitution of unknown, unidentified, and unlabeled samples in laboratories using EDXRF analysis



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A B S T R A C T

This Study presents a method to recover and label unknown samples in a nuclear laboratory using Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry based on spectra differentiation and analysis. This method was found to be a new powerful tool that can be used in different laboratories where a certain number of samples cannot be identified because they have never been identified, their labeling and identification cannot be assessed because of degradation, and/or any other causes. The method was found to be simple, timely appropriate, not expensive, and powerful in identifying and recover the information needed for a sample. The EDXRF spectrometry method for recovering unknown samples in laboratories was based on the following three main points:

- EDXRF method allows the elemental characterization of any sample without clear identification in a laboratory;
- The displaying of several samples' spectra on the same graph allows direct comparison and identification when the sample's data overlap one of the stored data; and
- The identification of the unknown sample based on the EDXRF results: The faster method being the overlapping comparison while the elemental characterization-based identification needs high skilled expertise in X-ray fluorescence analysis.

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Specification Table

Subject area:	Environmental Science Applied Nuclear Science Radiation source and detection
More specific subject area:	Environmental science
Method name:	EDXRF for recovering the unknown samples
Name and reference of the original method:	This is a new method that has never been published yet
Resource availability:	Data will be made available upon request
Main purpose:	Identify as a whole, an unidentified, unknown, or unlabeled sample in a laboratory using EDXRF spectrometry (Not to characterize the sample contain, though it is possible)

Method overview

In recent decades, the investigation of material properties through samples' analysis has grown in many applications such as space science, environmental monitoring, physical, chemical, geological, and biological sciences and techniques. The advancement of science and technology makes it easy to implement laboratories at international levels, national scale, and local or regional. Most of the environmental laboratory are subjected to sample characterization, and one of the main issues encountered is the timeframe of sample conservation and data archive. Because of the large number of samples, the changing of staff, the data storage, and the archive arrangement, it sometimes happens that one needs to recover the nature and origin of an unlabeled sample found in the laboratory or storage room before managing it (reclassification, reuse, or disposal either as ordinary waste, chemical or nuclear one). For this reason, many laboratories have developed a non-documented strategy to solve this issue and it is hard to fix such issues in new laboratories and/or by new laboratory technicians with little experience in the field.

The common issue raised in the previous paragraph could be fixed by a cheap and rapid method of samples' identification. Among the suggested methods at the Laboratory of Radioanalysis and Spectrometry of the National Radiation Protection Agency (NRPA), the visual inspection is the fastest and cheapest, but less accurate (high uncertainties and not fully based on scientific investigations) as it gives only visual aids, without technical and specific details. This visual inspection is followed by the Energy Dispersive X-Ray Fluorescence (EDXRF) as rapid and cheap. The EDXRF spectrometry [1–3] is a non-destructive nuclear method used to characterize samples in the view of their elemental composition. EDXRF spectrometry is applicable for production quality control, ecological environment monitoring, geological surveying (including the applications of μ -EDXRF), food safety, and heritage analysis, among others [4,5]. The method is being used worldwide because of its robustness, fast screening, and the possibility to be used in-situ and with different matrices [6–9]. The present research aims to describe the method named “EDXRF for recovering the unknown samples” being documented or published for the first time. EDXRF for recovering the unknown samples is the characterization and recovering of samples that may be found in any laboratory without being labeled or clear identification. Usually, such samples pose issues of management as follow:

- Their real value cannot be accessed unless one knows the purposes they were made for in the laboratory;
- Their usefulness needs to be properly defined prior to their disposal/classification, reuse as reference material if possible, or thrown away as laboratory waste; and
- When disposed of, their classification as waste needs to be defined prior to their release into the environment as it could be one of the main pollutants (heavy metal, radioactive, or chemical toxic).

The most appropriate and useful method to identify unknown samples in a laboratory should have some basic requirements. The method should be rapid as it is not for the main purpose of the laboratory. For instance, in a gamma-ray or alpha particle laboratory spectrometry, the main focus is likely on assessing environmental samples and determine their radioactivity concentration, instead of recovering unknown samples. It is also important to recall that gamma-ray spectrometry is a non-destructive technique commonly used to gauge electromagnetic radiation in the gamma-ray spectrum of radioactive sources or other nuclear materials [10–13]. The *EDXRF for recovering the unknown samples* hereby, is referred to as the technique used to unveil the hidden identity of unlabeled samples in the laboratory using Energy Dispersive X-Ray Fluorescence Spectrometry. When a sample is not identified by visual inspection and as per the previous two conditions the proposed method of identifying unknown/unlabeled samples should be clear, precise, and concise. The proposed method can be done in less than five minutes and analyzed in few minutes. The following algorithm depicted in Fig. 1 describes the method as being reproducible in other laboratories. The algorithm implementation starts after the visual inspection of the unknown/unlabeled sample is unsuccessfully done.

Method details

The method details are summarized in the previous algorithm presented in Fig. 1. Concerning the algorithm, it is appropriate to set a description of a reproducible method in terms of diagram, and that is the reason for developing this algorithm. It started when one has unidentified and/or unlabeled samples in the laboratory and needs to decide on its use, management, reclassification, and/or disposal. The present method, by being rapid, is based on Energy Dispersive X-Ray Fluorescence analysis (EDXRF). The following steps are to be taken while dealing with such samples and recovering them using X-Ray Fluorescence spectrometry. One should notice the importance of visual inspection prior to the application of these steps as it is a powerful tool used in laboratories every day. When the identification of an unknown/unlabeled sample failed under visual inspection, the following steps must be applied in this order.

Step 1: stamp new Id on the unknown and unlabeled samples (UNKNOWN-XX can be used or an abbreviation where XX is the numbering related to the sample under investigation). Such identification is of higher value especially when there are many unidentified/unlabeled samples in the laboratory. This is temporary labeling since, at the end of the process, a new stamp with the appropriate identification will be affixed on the sample. This step includes the samples in different forms as the management of liquid, solid (powder/ glass disc or pressed pellet) mainly, and the management of gas samples differ slightly. Gas samples are usually not store for a long time and the EDXRF method is complex to recover such unlabeled sample.

Step 2: unlabeled sample preparation. This step includes the activities to be done prior to the spectra acquisition. Usually, when the samples are well-conditioned and stored, the analysis can be done without another full sample preparation. This is recommended for unknown samples recovering but not for accurate elemental characterization of samples for another purpose. If the samples are not well stored and conditioned, the moisture content might have affected its content and a new simple preparation and conditioning are needed. If the sample is a glass disc prepared with additional fluxes added, it is difficult to recover accurately the detail at the time the samples were prepared since the degradation of the matrix after such preparation is time-dependent: so a routine check could reveal the hidden information. But the method is accurate to recover solid unknown samples at a rate of about 98 %. The preparation method for Energy Dispersive X-Ray Fluorescence spectrometry was described by Guembou et al. [1–3] and many other authors [7,8]. Prepared samples are disposed on the plate for spectrometer analysis (or on the rack depending on the type of spectrometer used) and fixed in the spectrometer chamber as depicted in Fig. 2.

Step 3: spectra acquisition. The temporary labeled unidentified (UNKNOWN-XX) samples are exposed to X-ray machine. The one used in our laboratory is the SPECTRO XEPOS model with different ranges of excitation energy. The process allows to collect spectra of the samples under investigation, stored them in the appropriate folder with appropriate information of the Laboratory and measurement conditions. The anode material of the X-ray tube used is made of an alloy

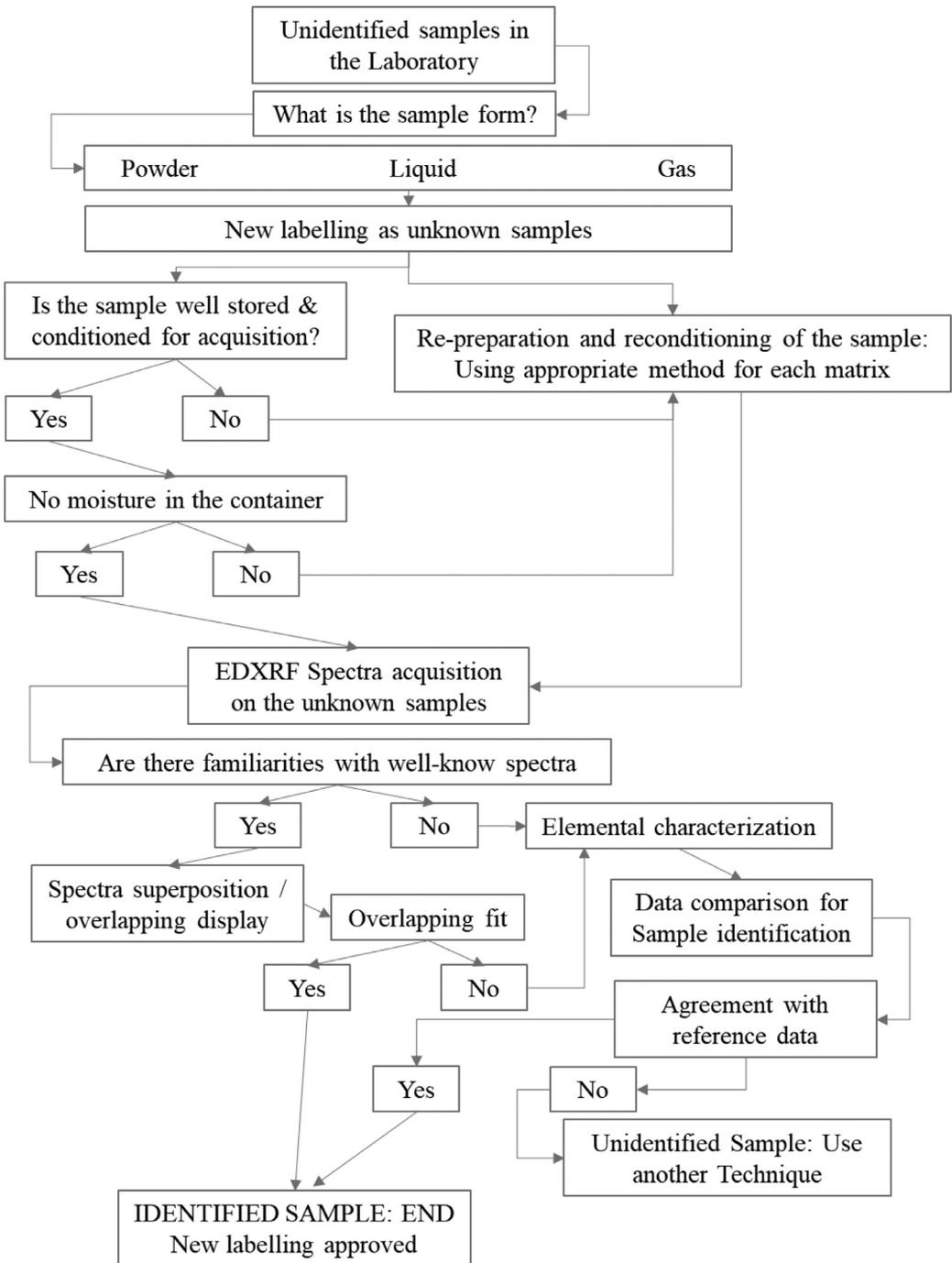


Fig. 1. Algorithm of the method EDXRF for recovering unknown samples in the laboratories. In most cases, when an XRF expert analyses the data at the latest stage of the method, the identification of the unknown samples is obvious.



Fig. 2. Spectro Xepos spectrometer with a sample plate of 12 positions disposed of for EDXRF analysis. The first two positions on the plate are reserved for calibration samples and other positions for the samples under investigation.

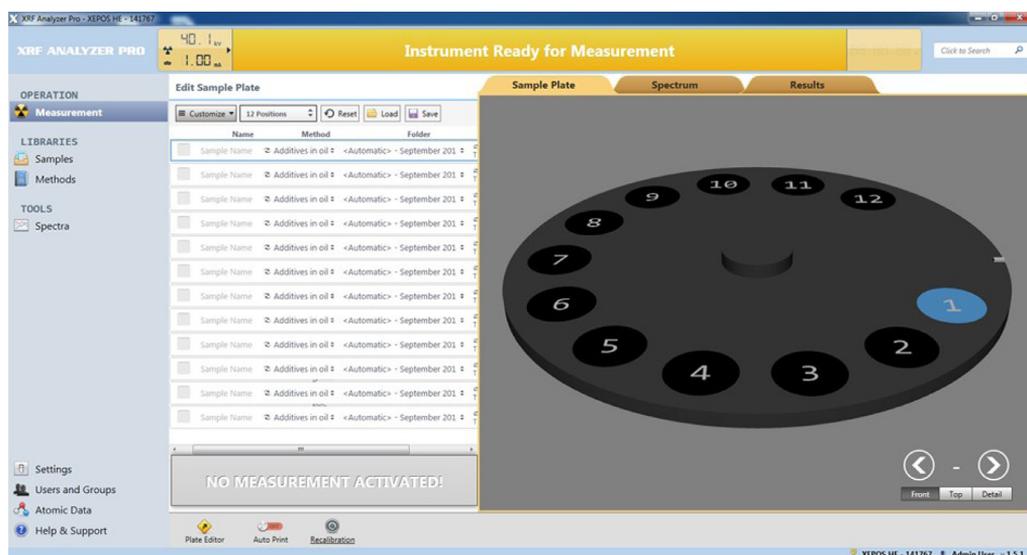


Fig. 3. Interface display of the XRF ANALYZER PRO used for spectra acquisition and data analysis. Details such as analytical method, sample name, folder, sample's mass, ... etc. are provided in the software.

of Palladium and Cobalt. The measurements were performed under air condition with a relative deadtime of 16.5 %, a zero peak rate of 2×10^7 CPS. The detector is a silicon drift detector with 4096 channels, its operating temperature is set to -30^0 C and its resolution (FWHM) is 133.8 eV at 5.89 keV (Mn $K\alpha$). The spectra on different samples are acquired with four energy ranges as listed below:

- $E < 3$ keV where the voltage is 22.6 kV and the current is 1.781 mA;
- 3 keV $< E < 6$ keV where the voltage is 22.6 kV and the current is 1.781 mA;
- 6 keV $< E < 19$ keV where the voltage is 45.2 kV and the current is 0.889 mA;
- 19 keV $< E$ where the voltage is 50.2 kV and the current is 0.799 mA.

Once the samples have been disposed of in the X-ray chamber, one can open the XRF ANALYZER PRO and launch the MCA calibration to set the calibration data up to date and assign each sample's position on the sample plate to the corresponding one on the software as can be seen in Fig. 3. After

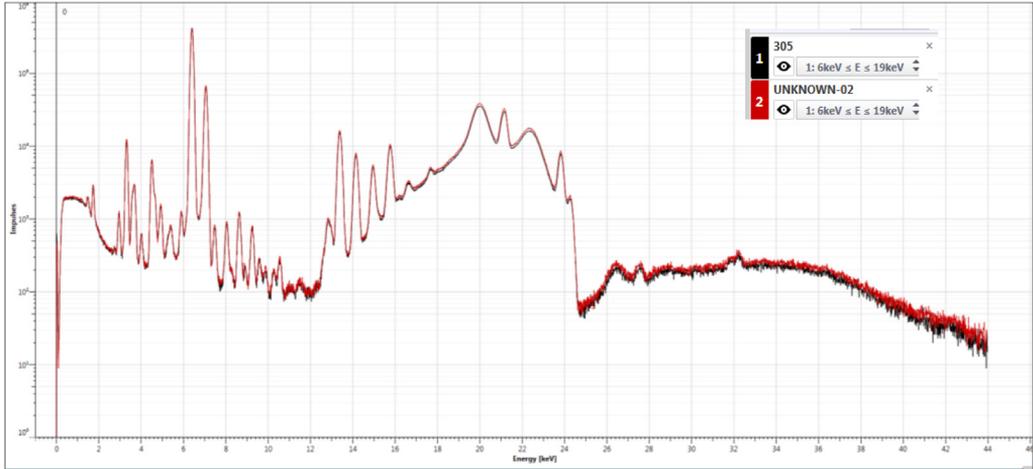


Fig. 4. Identification of an unlabeled and unknown sample in the laboratory using spectra overlapping display on the same graph. The spectra of the unknown sample fits well that of one reference material named “305” in our laboratory.

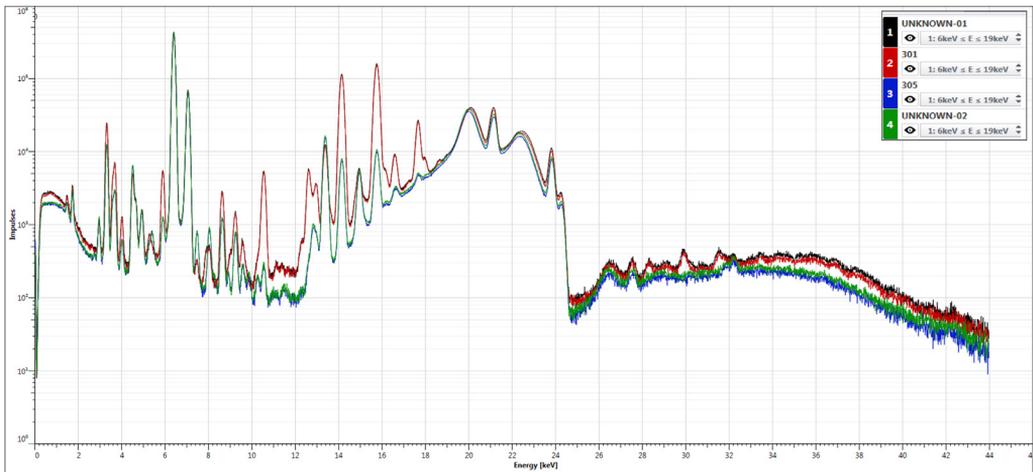


Fig. 5. Spectra overlapping display after comparison of the elemental composition of investigated samples with appropriate material. The unknown samples could now be identified as reference material named “301” and “305”.

filling in all the details regarding the method and the samples, the measurement can be performed and the spectra will be saved in the appropriate folder.

Step 4: data analysis. The first stage of this step consists of visual analysis of the picks in the spectra. When the laboratory scientist is familiar with the spectra of commonly used reference material in the laboratory, he can proceed by elimination and compared the spectra of the unknown samples only with the suspected fit samples. The displaying of the spectra obtained with the library stored in the computer allows an easy decision-making process in recovering the identity of the sample under investigation (Fig. 4). The visual interpretation of the spectra reduces the work of investigation and allow the experimenter to shortcut to the validation by comparing the obtained data to the suspected spectra directly. The second stage is when one is not familiar with the spectra. The overlapping display of the spectra on the same graph could lead to wasting of time and complex

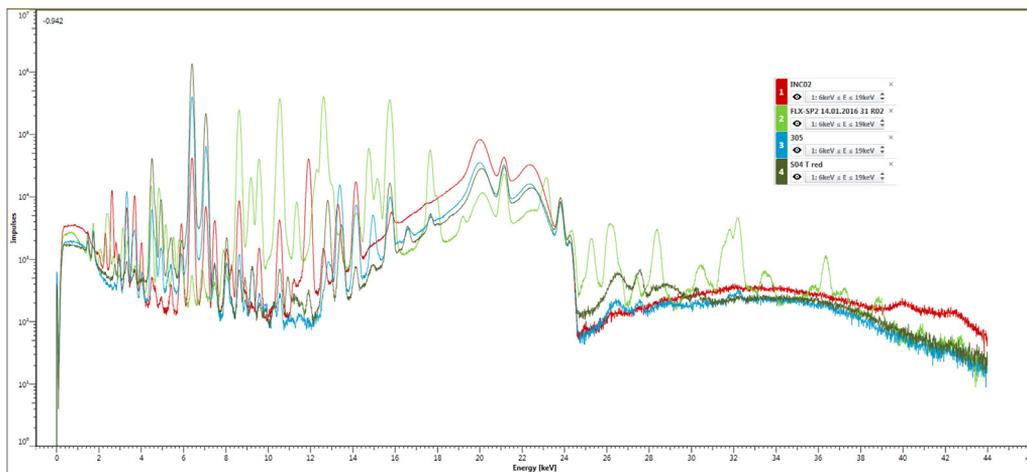


Fig. 6. The display of unfamiliar spectra with reference data of the laboratory. Non-overlapping of the spectra, suggesting unidentified unknown samples based on spectra comparison.

identification of the unidentified sample as can be seen in Figs. 5-6. Thus, this stage requires an elemental characterization of the unknown samples based on spectra analysis prior to the data comparison. The comparison of the elemental composition of the investigated samples with that of other materials previously analyzed in the laboratory or certified by other institutions could probably lead to the identification of the sample.

The method being used here was described in the paper entitled “determination of the natural radioactivity, elemental composition and geological provenance of sands from Douala in the littoral region of Cameroon using X-ray and Gamma-ray spectrometry” published in 2019 by Guembou et al. [1]. The method combines low background with high sensitivity to achieve low detection limits, calculated using the following equation [1,14,15]:

$$LOD = 3 \times C_0 \frac{\sqrt{B}}{N}$$

where LOD is the limit of detection; N refers to the counts of an element-specific line of a standard within a region of interest (ROI) having a width of $1.1 \times FWHM$; B refers to the background in the same ROI as the element line; and C_0 is the concentration of the observed element in the reference sample. The software calculates the standard deviation related to the equipment performance, but the manipulator should remember the deviation from other steps as sample preparation and mainly weight measurements. The following figure (Fig. 4) describes the case where the manipulator, after a visual analysis of the spectra, suspected the unknown sample under investigation to be the reference material, the so-called “305”. By displaying both spectra on the same graph, it becomes easy to confirm the identity of the unknown sample and it could be re-labeled accordingly and go through its management decision process.

While a sample's spectrum cannot be easily recognized, it is recommended to perform an elemental composition analysis and the results are displayed as shown in the following figure. The identity of most of the samples investigated at this stage will be unveiled: For solid /powder samples, almost 98 % will be recovered and for liquid samples, about 90 % will be labeled at the end of this stage. The data shown in Tables 1 and 2 are two cases of recovering solid/powder samples in the lab using the present method.

At the end of this step, when an unknown sample cannot be identified, it is appropriate to make a decision or to use another appropriate characterization technique such as DRX, Laser spectroscopy, ... etc for decision management [16–20]. One example is that a routine gamma-ray spectrometry measurement [12,21–23] on the sample will reveal if it is a radioactive material that could not be

Table 1

Elemental composition of major elements/compounds from the investigated UNKNOWN samples along with Standard reference materials 1-8 used in the Laboratory. The standard materials referred to here are materials present in the laboratory with known elemental composition and clear identification.

Element	Method	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂	K ₂ O	CaO	MnO	Fe ₂ O ₃
STD1	TQ powders and liquids Air	4.88 ± 0.1	37.88 ± 0.1	46.58 ± 0.05	0.619 ± 0.004	0.352 ± 0.002	0.656 ± 0.001	3.251 ± 0.002	1.136 ± 0.22	6.384 ± 0.004
STD2		2.04 ± 0.06	31.89 ± 0.09	59.62 ± 0.06	0.639 ± 0.004	0.192 ± 0.001	0.714 ± 0.001	3.622 ± 0.002	1.162 ± 0.22	6.117 ± 0.003
STD3		2.5 ± 0.07	44.66 ± 0.1	47.04 ± 0.05	0.572 ± 0.003	0.095 ± 0.001	0.662 ± 0.001	2.181 ± 0.001	1.046 ± 0.22	5.705 ± 0.003
STD4		3.59 ± 0.09	38.2 ± 0.09	51.6 ± 0.05	0.701 ± 0.004	0.278 ± 0.002	0.859 ± 0.001	3.083 ± 0.002	1.161 ± 0.22	5.914 ± 0.003
STD5		2.34 ± 0.07	44.85 ± 0.1	31.15 ± 0.04	0.597 ± 0.004	0.345 ± 0.002	0.623 ± 0.001	4.343 ± 0.002	0.949 ± 0.22	6.01 ± 0.003
STD6		2.46 ± 0.07	40.74 ± 0.1	49.69 ± 0.05	0.693 ± 0.004	0.137 ± 0.001	0.87 ± 0.001	2.886 ± 0.002	1.333 ± 0.22	6.186 ± 0.003
STD7		3.11 ± 0.06	37.02 ± 0.08	56.12 ± 0.05	0.60 ± 0.003	0.152 ± 0.001	0.719 ± 0.001	2.141 ± 0.001	0.891 ± 0.176	4.801 ± 0.003
STD8		3.9 ± 0.08	39 ± 0.09	50.93 ± 0.05	0.837 ± 0.004	0.136 ± 0.001	0.772 ± 0.001	2.349 ± 0.001	1.239 ± 0.22	5.793 ± 0.003
STD9		3.71 ± 0.09	43.07 ± 0.1	45.49 ± 0.05	0.513 ± 0.003	0.200 ± 0.001	0.791 ± 0.001	2.761 ± 0.001	1.108 ± 0.22	6.058 ± 0.003
STD10		2.33 ± 0.07	33.8 ± 0.09	56.57 ± 0.05	1.689 ± 0.005	0.408 ± 0.002	0.793 ± 0.001	2.756 ± 0.001	1.128 ± 0.22	6.558 ± 0.003
UNKNOWN-1	3.8 ± 0.09	43.6 ± 0.1	45.97 ± 0.05	0.564 ± 0.003	0.188 ± 0.001	0.736 ± 0.001	2.82 ± 0.001	1.068 ± 0.22	5.966 ± 0.003	
UNKNOWN-2	3.08 ± 0.07	36.82 ± 0.08	55.98 ± 0.05	0.599 ± 0.003	0.148 ± 0.001	0.711 ± 0.001	2.138 ± 0.001	0.903 ± 0.176	4.634 ± 0.003	

Table 2

Colorful discrimination of element/compounds used to identify the unknown sample number 2. The unknown sample was characterized as being the closest material to STD7 standard reference material.

Element	Method	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂	K ₂ O	CaO	MnO	Fe ₂ O ₃
STD1	TQ powders and liquids Air	4.88 ± 0.1	37.88 ± 0.1	46.58 ± 0.05	0.619 ± 0.004	0.352 ± 0.002	0.656 ± 0.001	3.251 ± 0.002	1.136 ± 0.22	6.384 ± 0.004
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STD5		2.34 ± 0.07	44.85 ± 0.1	31.15 ± 0.04	0.597 ± 0.004	0.345 ± 0.002	0.623 ± 0.001	4.343 ± 0.002	0.949 ± 0.22	6.01 ± 0.003
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STD8		3.9 ± 0.08	39 ± 0.09	50.93 ± 0.05	0.837 ± 0.004	0.136 ± 0.001	0.772 ± 0.001	2.349 ± 0.001	1.239 ± 0.22	5.793 ± 0.003
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UNKNOWN-2		3.08 ± 0.07	36.82 ± 0.08	55.98 ± 0.05	0.599 ± 0.003	0.148 ± 0.001	0.711 ± 0.001	2.138 ± 0.001	0.903 ± 0.176	4.634 ± 0.003

Table 3

Colorful discrimination of element/compounds used to identify the unknown sample. The unknown sample number 1 was characterized as being the closest material to STD9 standard reference material.

Element	Method	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂	K ₂ O	CaO	MnO	Fe ₂ O ₃
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released in the environment (but radioactive material and rarely unlabeled and unknown because of their strict management worldwide). Table 1 shows the elemental composition of reference samples analyzed along with the two unknown samples under investigation in the present work. It is appropriate to use a comparative tool as Excel SPSS-Statistic, or Matlab code to draw out the closest reference samples to unknown samples as can be seen in Tables 2 and 3.

If the previous data are lost because of both an issue with the computer and the unlabeled sample, the same method should be used as the characterization of the unknown sample need to be done by analyzing the sample. Step 4 could be implemented directly by skilled manipulator in the laboratory Figs. 5–7.

Conclusion

The present study suggested a new method to recover unknown, unlabeled, and unidentified samples in a laboratory using the Energy Dispersive X-Ray Fluorescence spectrometry technique. The method was proven to be prominent and its usefulness and accuracy in revealing the identity of the samples under investigation were demonstrated in the laboratory. While the algorithm developed for the present study is new and could be extended to other methods, attention should be paid to the risk-related to different samples' management due to their forms (liquid, solid-powder, and gas) and physical and chemical properties (hazardous materials).

The method could be used in any other laboratory as the algorithm presented to summarize it was tested many times in our laboratory. The elemental analysis using EDXRF allows material composition, characterization and this reveals the nature of a sample in comparison to others. In addition, when

Results	Loss on Ignition -2.9996 %
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The error is the statistical error with 1 sigma confidence interval

	Element	Concentration	Abs. Error
12	MgO Magnesiumoxide	3.458 %	0.095
13	Al ₂ O ₃ Aluminumoxide	45.89 %	0.09
14	SiO ₂ Siliconoxide	44.20 %	0.05
15	P ₂ O ₅ Phosphorusoxide	0.5128 %	0.0036
16	SO ₃ Sulfideoxide	0.1980 %	0.0011
17	Cl Chlorine	0.06513 %	0.00028
19	K ₂ O Potassiumoxide	0.6691 %	0.0009
20	CaO Calciumoxide	2.968 %	0.001
22	Ti Titanium	5084 µg/g	3
23	V Vanadium	92.6 µg/g	1.1
24	Cr Chromium	87.1 µg/g	0.4
25	MnO Manganeseoxide	1027 µg/g	1
26	Fe ₂ O ₃ Ironoxide	5.424 %	0.003
27	Co Cobalt	< 9.3 µg/g	-
28	Ni Nickel	61.1 µg/g	0.8
29	Cu Copper	857.2 µg/g	2.3
30	Zn Zinc	603.6 µg/g	1.6
31	Ga Gallium	15.9 µg/g	0.3
32	Ge Germanium	0.4 µg/g	0.2
33	As Arsenic	3.2 µg/g	0.3
34	Se Selenium	< 0.2 µg/g	-
35	Br Bromine	3.1 µg/g	0.1
37	Rb Rubidium	21.2 µg/g	0.2
38	Sr Strontium	71.4 µg/g	0.2
39	Y Yttrium	10.0 µg/g	0.2
40	Zr Zirconium	285.0 µg/g	0.5
41	Nb Niobium	20.7 µg/g	0.2
42	Mo Molybdenum	4.5 µg/g	0.4
44	Ru Ruthenium	< 0.7 µg/g	-
45	Rh Rhodium	< 0.1 µg/g	-
46	Pd Palladium	< 0.7 µg/g	-

Fig. 7. Data analysis of the elemental characterization of the unknown sample in view of its identification. Data are exported in an Excel sheet and can be analyzed side to the database available either in the laboratory or in the reference material manufacturers or standards provider. Most of the data can be found on NIST or SRM webpages.

familiar with spectra visual analysis, one could easily identify the unlabeled unknown sample and confirm by displaying several suspected spectra on the same graph. This was presented accordingly in the present method research.

Declaration of Competing Interest

The authors declare not conflict of interest.

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