Scientists improve an X-ray fluorescence analysis algorithm

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Scientists from the Faculty of Chemistry of the Lomonosov Moscow State University have performed computations and derived new equations to conduct X-ray fluorescence analysis with higher accuracy in comparison to current algorithms. This method doesn't require a large number of reference materials and operates with complex composition samples. The chemists have represented their research in the journal *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*.

X-ray fluorescence analysis (XRF analysis) is a method for detecting the chemical compositions of substances. This technique is based on measurement and analysis of spectra from X-ray irradiation. When interacting with photons, atoms of the reference material become excited, after which they return to their ground state. During irradiation, every atom emits a photon with definite energy, which provides chemists information about the substance structure.

X-ray tubes are often used as a radiation source. Reference materials with known composition allow researchers to determine element content from measured radiation intensity. One of the unsolved X-ray fluorescence analysis problems is the presence of a substantial amount of light elements (II-III periods of Mendeleev periodic system) in many real samples. Very often, radiation of these light elements can't be registered. X-ray fluorescence radiation of light elements is referred to as soft (long-wave) radiation, so researchers can't use salt crystals to analyze radiation wavelength, since distances between planes where atoms of these crystals lie are too small.

At the same time, ordinary diffraction gratings, namely optical devices composed of a set of regularly situated slits are also unsuitable. The reason is that they are appropriate for radiation with a wavelength of about tens or hundreds of nanometers, rather than radiation with the wavelength of several nanometers. So the only solution is to use expensive synthetic multilayer mirrors, which are not available in every spectrometer.

There is also a fundamental problem of low fluorescence yield of light elements. This means that very powerful X-ray tubes are necessary, leading to cost increases. Moreover, such processes are more complicated than those for excitation of heavy elements, and aren't studied as well, so traditional X-ray fluorescence analysis techniques don't guarantee good results all the time.

Andrey Garmay, a doctoral student at the Analytical Chemistry Department at the Faculty of Chemistry of the Lomonosov Moscow State University and one the project authors, says, "There are three difficulties with oxygen, carbon and other light elements: one technical and two fundamental. You need expensive devices for solving the first and second problems and fundamental physical research to solve the third one. Nowadays, indirect methods of determination of light elements' content are cheaper and more accurate, even when good equipment is available. That's why we are also proceeding in this very direction."

Also difficulties emerge in case of different nonstandard objects, for instance, technological products of complex shape, if it's not easy to find appropriate reference materials for them. At the same time the most accurate analytical techniques work in narrow ranges of samples compositions and often require dozens of reference materials.

Garmay says, "Taking into consideration the experience of XRF analysis, rather than absolute intensities of elements' radiation, we use their ratios and also the ratio of intensities of X-ray tube characteristic radiation, coherently (without wavelength change) to incoherently (energy of a part of scattered photons is less than energy of initial beam quanta) scattered by a sample. We've managed to derive new equations to conduct analysis with equal or even higher accuracy than existing algorithms. At the same time, these equations require no more than one or two reference materials and could operate in wide ranges of sample compositions."

The scientists began to use an internal standard method in order to neutralize the impact of experimental factors, changing from one measurement to another, on analytical response. Thus, these factors, influencing two close signals in spectrum approximately identically, compensate each other and measurement error becomes lower when ratios of these signals are used. The chemists used computations in order to become less dependent on expensive standard samples and operate in wider ranges of sample compositions.

Moreover, the method elaborated by the chemists has turned out to be the only one suitable for analysis of nonstandard objects with high content of undetected light elements in the absence of adequate reference materials.

Garmay says, "Initially, we were looking for some tools to improve accuracy of steel sample analysis, but later, faced a problem of oxide material analysis. And since our spectrometer couldn't register oxygen radiation, we had to look for other means, starting out from existing techniques. We've studied fundamental equations, connecting intensities of characteristic and scatter radiation with composition of reference materials and derived new simplified formulas for our analysis."

In the course of the work, the scientists measured spectra of high-alloy steel samples, iron-ore material samples and a powder blend of metal oxides with known composition. Using the new approach, along with other well-proven XRF analysis techniques, the chemists conducted analyses and assured themselves of that the elaborated tool produces more precise results, especially in the absence of adequate reference materials.

The scientists still need to prove experimentally that their method is applicable for determination not only of IV period elements, but also of heavier elements. Besides that, the researchers are going to optimize the analysis procedure and make it easier without loss of accuracy.

Andrey Garmay says, "In the long term, we are going to check if it's possible to estimate the qualitative composition of undetected light elements, judging by the wavelength distribution of bremsstrahlung radiation of an X-ray tube, scattered by a sample. This could make our method more universal."

More information: Andrey V. Garmay et al, Improving accuracy and capabilities of X-ray fluorescence method using intensity ratios, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* (2017). DOI: 10.1016/j.nimb.2017.02.072

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