White paper

IonicX Portable XRF Analyzer Device and Algorithm

A detailed look into the algorithm used to authenticate ionic salts

The Thermo Scientific™ IonicX™ Portable XRF Analyzer utilizes Energy Dispersive X-ray Fluorescence (ED XRF) spectrometry to confidently differentiate between different chemical samples based on their atomic structure and the average atomic weight of the sample. The basic elements of XRF spectrometer systems include a radiation source, a sample, and an X-ray detector. The analysis relies on the interaction of radiation source output (an X-ray source) with a sample, in this case, the cup of ionic salt material, such as Sodium Chloride, Potassium Chloride, Sodium Hydroxide or other chemicals and salts. The XRF system can characterize materials, due to the fundamental principle that each element has a unique atomic structure, which in turn has a unique set of peaks (x-ray lines) in its emission spectrum. The energy dispersive X-ray detector separates (disperses) the detected radiation emitted from the sample by energy, thus providing a spectrum from which the different elements present in the sample can be identified and/or quantified.

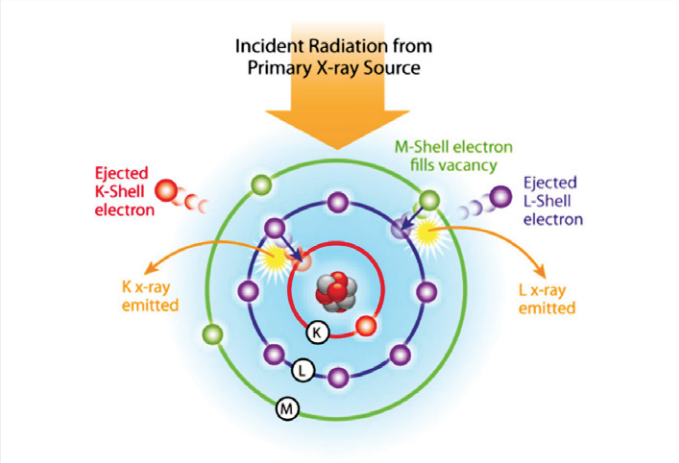

Figure 1. Stimulation of characteristic XRF emission lines.

Principles of XRF

To stimulate the emission of X-rays from a sample, a beam of high energy photons (X-rays), is focused on the sample. When X-rays strike an atom, there are three possible primary interactions. The most widely used in XRF spectrometry is the secondary emission arising from photoelectric absorption where the incident beam from the X-ray tube is absorbed by the atom and causes the ejection of an inner shell electron (primarily K & L shells), while creating an electron-hole where the electron was located. An electron from an outer higher-energy shell then quickly fills this vacancy. In this process, an X-ray photon corresponding to the difference in energy of the inner and outer shell is emitted. This emitted X-ray is captured by a semi-conductor detector, and its peak energy is specific to the element from which it was emitted. These X-rays are also referred to as characteristic X-rays. This process is shown in Figure 1.

The second form of interaction is called coherent scatter, or Rayleigh scatter. Coherent scatter occurs when the incident X-rays scatter from a whole atom or a group of atoms, resulting in a change in the direction of the X-ray's travel, but no change in the X-ray's energy. Often this occurs when the incident X-ray beam is scattered by the electron cloud of an atom. The coherent portion of the scatter spectrum essentially mirrors the incident spectrum; it contains the same characteristic energies emitted from the analyzer's X-ray tube and the Rayleigh scattered x-ray tube continuum (Bremsstrahlung) contributes to the background of the sample spectrum. Rayleigh scatter intensity increases with increasing atomic number, e.g. there is less Rayleigh scatter for low Z atoms, such as carbon and more Rayleigh scatter for high Z atoms, such as lead. (Here, "Z" refers to the atomic number of an element.)

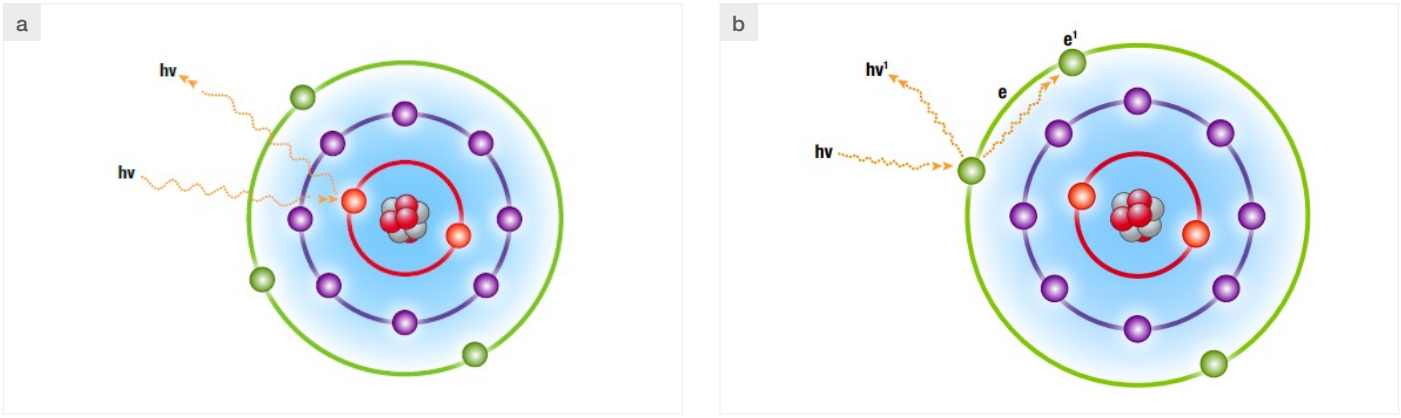

Figure 2. a) Rayleigh scattering: A scattered photon has same energy as an incident photon b) Compton Scattering: A scattered photon has the energy of the incident photon less the kinetic energy of the interacting electron.

The third most common form of x-ray interaction is incoherent scatter, or Compton Scatter. Compton scatter from a free or loosely bound (outer shell) electron, causes the transfer of a relatively small portion of the X-ray's energy to the electron, so the incident X-ray's energy is shifted (slightly) toward lower energy. As some of the incident X-ray energy is lost through the scatter process, the incoherently scattered X-rays are measured in the spectrum at slightly lower energies from their initial energy. For example, an Ag-target X-ray tube's Ag-La1 characteristic line (22.16 KeV) shows up in the incoherent portion of the scattered spectrum at around 20.6 KeV. As an X-ray tube emits not only characteristic X-rays from the anode but also broad band X-rays from Bremsstrahlung radiation, the scattered X-ray spectrum results in a continuum of scattered X-rays from low to high energy, depending upon the specific incident X-ray energy. Compton scatter tends to be inversely proportional to the mass attenuation coefficient of the analyzed material: there is more Compton scatter for low Z atoms, such as carbon and less Compton scatter for high Z atoms, such as lead.

As the Compton scatter changes with respect to the mass absorption coefficient, which itself depends on the element composition and density of the material, there is considerable information within the Compton scattering part of the spectrum to determine characteristic information about the sample. These scatter processes are shown in Figure 2.

A XRF spectrum example

Plotted below in Figure 3 is a spectrum of Potassium Chloride (KCl) taken with a silver X-ray tube with the excitation voltage set to 45kV. The spectrum has several X-ray fluorescence peaks associated with Potassium (K) and Chlorine (Cl). At 22 and 25 KeV the Ag Kα and Kβ lines can be seen in the spectrum. These are the Rayleigh scattered X-rays from the Ag anode in the X-ray tube scattered by the sample. The two broadened peaks to the left of the Ag Kα and Ag Kβ lines are the lower energy Compton peaks from the Ag-lines emitted by the X-ray tube. The broad spectral response between 18 to 45 KeV corresponds to the continuum emitted by the X-ray tube scattered through the sample via both Rayleigh and Compton scatter.

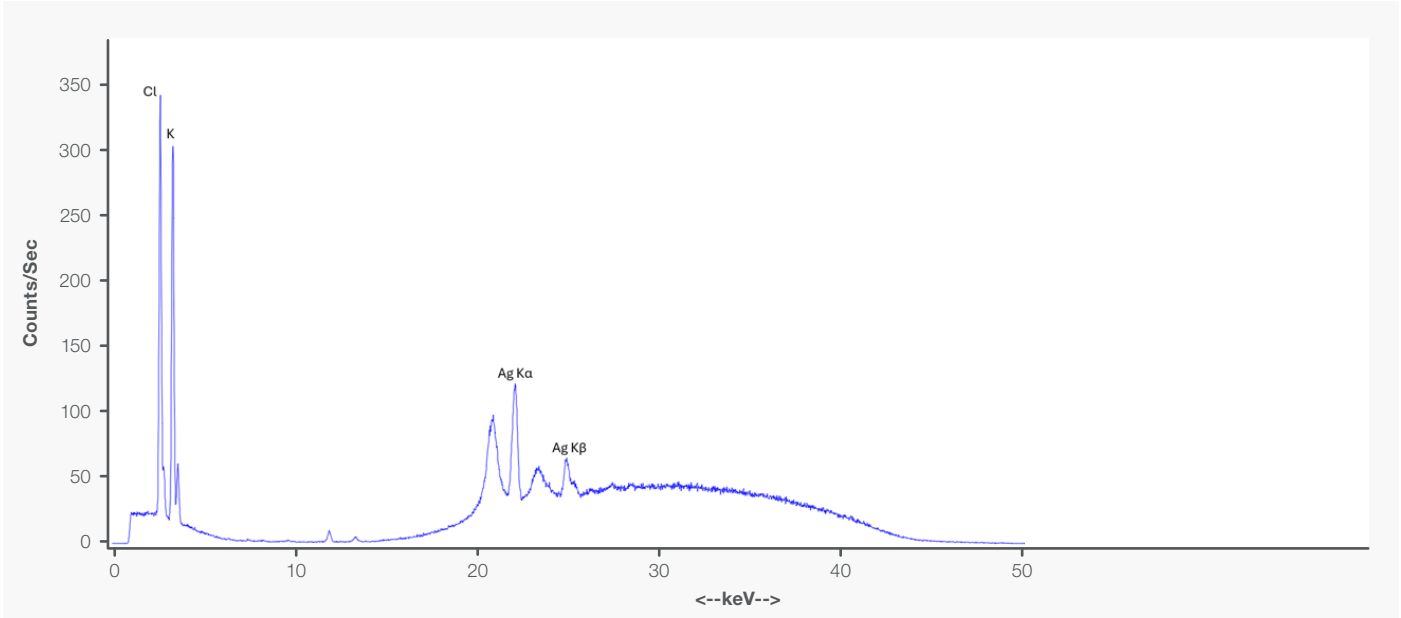

Figure 3. XRF spectrum of KCl sample.

Algorithm

Handheld XRF devices often cannot detect elements lighter than Magnesium by their fluorescence lines, however many compounds contain elements of interest such as Oxygen and Hydrogen. Additionally, relying solely on primary fluorescence peaks to identify target compounds can lead to misinterpretation. For instance, if MgO and NaCl are present in a 1:1 mixture, the resulting XRF spectrum would display distinct characteristic Mg and Cl peaks. However, the sample would not actually be the spectrum of $MgCl_2$, as the analytical response of Mg and Cl would be very different in both samples because of a dilution effect and absorption from Na and O atoms. The XRF process can easily differentiate samples with similar elemental constituents but with different chemical structures by analyzing the resulting scatter from the sample and comparing the full spectrum to a calibration library of compounds. Figure 4 shows XRF spectra of Sodium Chlorate ($NaClO_3$) and Sodium Perchlorate ($NaClO_4$) taken with the IonicX XRF instrument. In this example, only the Cl fluorescence peak can be detected by the IonicX device as Na and O fluorescence X-rays have energies that are too weak to be detected. However, when the spectrum is normalized, in this case to the primary Compton peak of Ag Kα, a slight but distinguishable difference can be seen in the spectral intensity between the energies of 25 keV and 40 keV. The difference in the scatter of the X-ray tube Bremsstrahlung is caused by differences in mass absorption coefficients of the presented samples, in this case it is the extra O atom in the $NaClO_4$ molecule vs the $NaClO_3$ molecule.

A least squares regression may be calculated by comparing one or more spectrum/spectra from a library of X-ray spectral signatures in the IonicX instrument to the spectral signature of an unknown sample. A perfectly matched sample spectrum to a library spectrum will have a slope of 1.0 and an intercept of 0. For example, a correlation score (C-Val) is calculated for each potential match using the square roots sum of squares for slope and intercept according to the equation C-Val = 1.0 – sqrt ((slope2) + offset2)). Each spectrum from the evaluation set is iteratively compared using a linear fitting model to each spectrum from the training set.

Analysis time is enhanced by first testing with a lower X-ray tube voltage. The lower voltage will produce fluorescence peaks from elements commonly found in salts such as: K, Cl, Mg, Ca and S. The elemental fluorescence enables pre-filtering the calibration library for ionic salts containing only the elements that were detected with any of their characteristic X-rays. For example, if the target compound is NaCl and the system does not detect a fluorescence peak from Cl, then the sample cannot be NaCl and therefore NaCl is eliminated from the list of potential matches. However, the presence of Cl does not mean the sample is NaCl. As a previous example showed, a mixture of MgO_2 and NaCl would have fluorescence peaks from Mg and Cl. IonicX is able to differentiate this sample from $MgCl_2$ using the primary algorithm described above. In this example where Mg and Cl were detected in the low-voltage pre-scan, the analyzer would perform a subsequent high-voltage scan and the primary algorithm would be employed to distinguish between a mixture of MgO_2 and NaCl versus a sample containing only $MgCl_2$ based on differences in the scatter region caused by the different mass absorption coefficients of MgO_2 and NaCl versus a sample containing only $MgCl_2$.

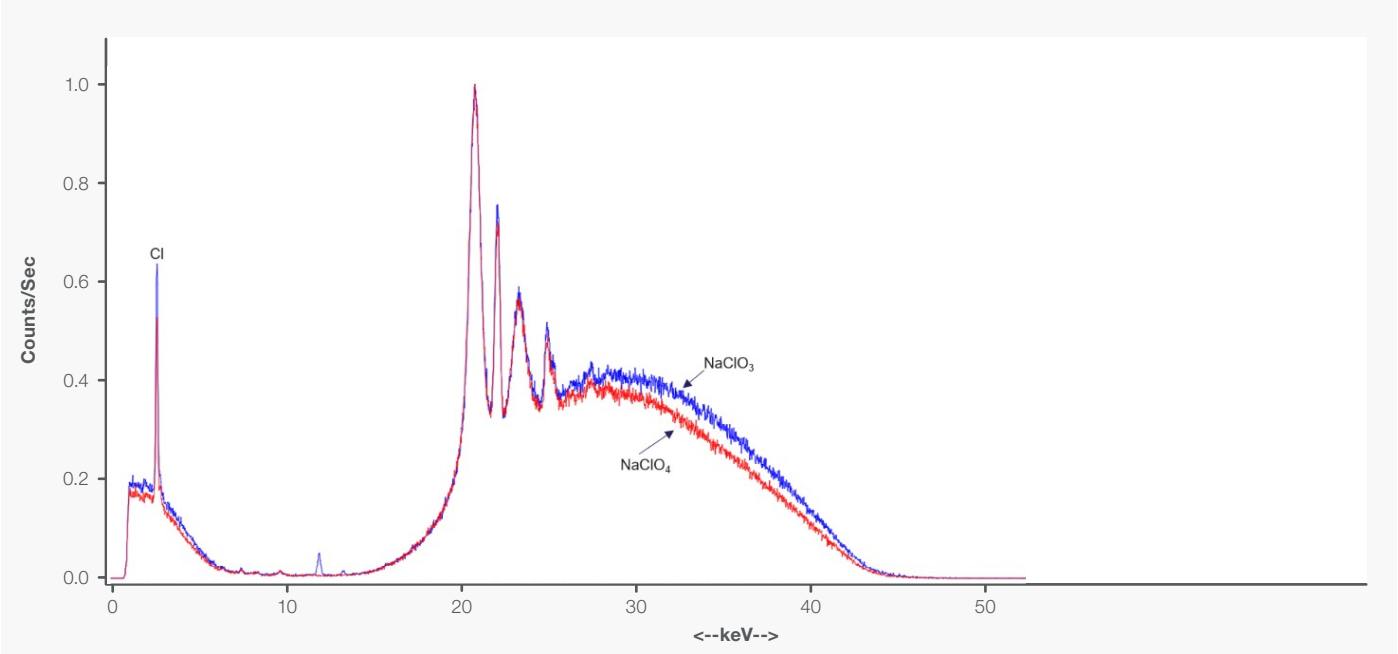

Figure 4. XRF spectrum of $NaClO_3$ and $NaClO_4$.

The current IonicX Portable XRF Analyzer algorithm supports the verification of multiple different chemicals including, but not limited to: NaCl, KCl, $MgCl_2$, $CaCl_2$ and NaOH. The IonicX device has shown excellent selectivity when challenging the device with those chemicals and associated methods. Figure 5 indicates the C-values for the five methods vs. five chemicals (challenges). When those methods are selected and challenged, a user can expect one of two clear unambiguous results, as shown in figure 6, a pass (i.e. C-value ≥0.7) or a fail (i.e. C-value <0.7).

Methods					
IonicX Challenge Samples	C-Values				
	NaCl	KCl	$MgCl_2$	$CaCl_2$	NaOH
NaCl	**0.94**	0	0	0	0
KCl	0	**0.96**	0	0	0
$MgCl_2$	0	0	**0.91**	0	0
$CaCl_2$	0	0	0	**0.83**	0
NaOH	0	0	0	0	**0.88**

Figure 5. C-values.

Summary

The IonicX Portable XRF Analyzer is a powerful addition for the verification of ionic salt type chemicals, utilizing XRF technology in a versatile, easy to use, small form factor. IonicX provides clear, easy to understand, unambiguous results and tools to assist with compliance and data integrity. IonicX is a robust verification tool which allows pharmaceutical companies to more efficiently verify incoming chemicals that typically have been tested using lengthy wet-chemistry techniques.

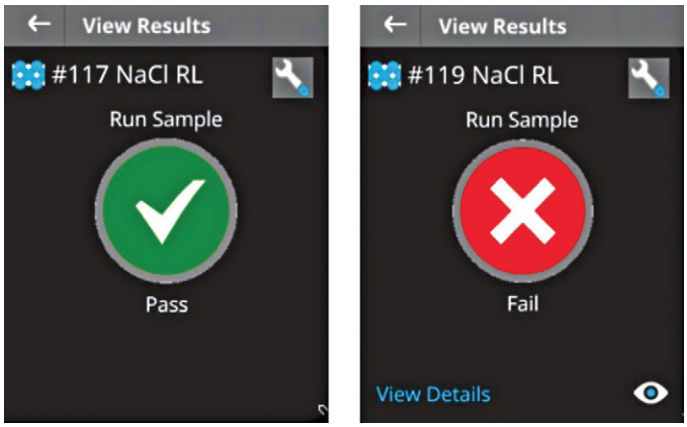

Figure 6. Results.

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