SciAps ApNotes
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Material Verification of Ionically Bonded Salts Using Handheld LIBS

Introduction

The food and pharmaceutical industries regularly utilize handheld analyzers based on either Raman or near-infrared (NIR) spectroscopy for chemical verification of raw materials. Raman and NIR technology, however, are both blind to ionically bound compounds including common salts like NaCl, KCl, chlorides, acetates, etc. Thus until recently there's been no effective handheld analyzer technology for verification of these materials.

SciAps has introduced a handheld analyzer, the Z-300, using laser-induced breakdown spectroscopy (LIBS). The Z-300 offers a fast, highly precise handheld technology for analysis of ionic salts. It fires a series of laser pulses onto a sample, creating a plasma. As the plasma cools, atomic emissions from material being analyzed are captured in a spectrometer, thus yielding the elemental concentration of the material. The analysis time is 2-3 seconds. The technique resembles spark optical emission, except a pulsed laser is used to generate the plasma rather than an electric spark. Thus, any sample may be analyzed, whereas spark OES requires a conducting material.

Analyzer Details

The Z-300 is capable of measuring any group of elements in the periodic table, from H to U. It features a wide range spectrometer (190 – 950 nm), an on-board, user-replaceable argon purge (for 10x improvement in precision compared to air-based analysis), and a rastered laser for obtaining averaged results over a typical sample area. The device is designed with an Android operating system yielding an easily upgradeable platform, and broad connectivity to other devices.

The Z measures H, C, Li, Na, Cl, Mg, Ca, K and other elements, allowing fast (2-3 s) verification of ionically bonded materials. It is highly sensitive to ionically bonded compounds unlike Raman and NIR. And the Z is very sensitive to the low atomic number elements such as H, C, O, Li, Na, Mg, Ca, K, S. LIBS is superior to handheld x-ray fluorescence (XRF) technology for this application. HHXRF is insensitive to elements Na and lower atomic number, and only weakly sensitive to key cations Mg, Al, Ca and K.

Test Results

Figure 1 shows the Z-300 spectra from store-bought sodium chloride (NaCl) and potassium chloride (KCl) materials. Figure 2 shows a region of the spectra for an NaCl sample. As shown in Fig. 1, both Na and K are very strong emitters. The main lines labeled as Na$_1$, Na$_2$, etc. The K line (K$_1$) at about 405 nm is generally not used for material analysis, because it suffers from a large,

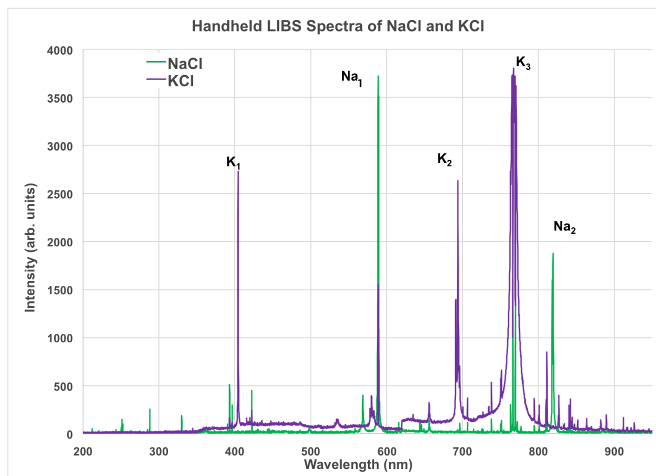

Figure 1.

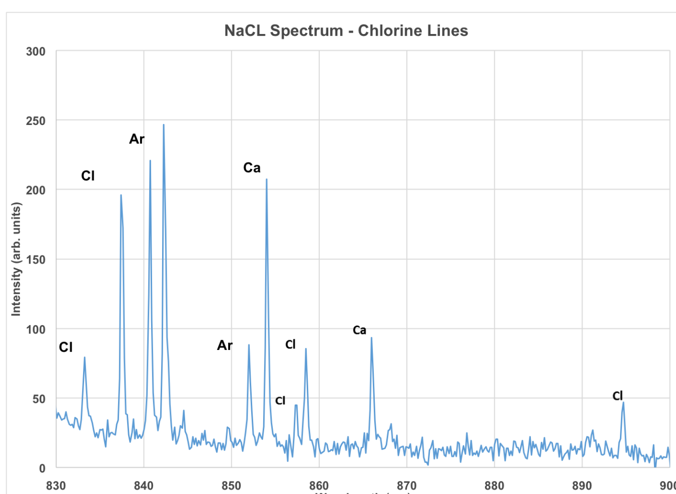

Figure 2.

> test results cont.

hard to correct interference if iron is present in the material. Instead the line at either K_2 or K_3, is used. K_2 is useful for analysis of K in materials that are mostly potassium based. The unusual shape of K_3 seen in Fig. 1 occurs because it is saturating due to the high potassium concentration in the sample tested. Thus K_3 is utilized for cases when lower concentrations or trace levels of K are measured. The same may be said of sodium. For high concentrations, the Na_2 line is used due to saturation of the Na_1 line in a more pure NaCl material. These store-bought materials did have contamination. There is Na measured in the KCl and K measured in the NaCl samples.

Figure 2 shows the expanded spectral region from 830 nm to 900 nm. This spectrum demonstrates how critical is the wide range spectrometer (out to 950 nm). Shown are the five unique chlorine (Cl) lines measured simultaneously with K, Na, Ca and other elements (also shown are the lines from the argon purge gas). First, a highly confident verification of NaCl requires that both Na and Cl be measured. A technique that relies only on Na may be fooled by sample contamination, or by a compound such as NaOH. Second, measuring multiple lines – 5 in the case of Cl – yields a statistically much higher confidence of validation, than measuring a single line. A spectrometer that spans into the 900 nm range is critical, especially for Cl. Finally, for many material verifications, sulfur must be measured. The Z-300 is the only HH LIBS analyzer that extends to 950 nm in order to measure the S emissions in the 920 nm region.

It's also important to note what elements are not measured. The Z-300 is very sensitive to hydrogen (H), emission at 656.5 nm, and moderately sensitive to O and N (emissions in the 700's nm range). These emissions do not appear, or produce very small signals, in the NaCl and KCl spectra because of the argon purge. The purge removes water-vapor containing air from the analysis area. For example, this is very important as the H and O measurements are a critical way to distinguish NaCl from NaOH. Both the argon purge and the high resolution, wide range spectrometer are critical. They provide the elemental range and sensitivity for definitive identification of ionically bonded salt compounds.

Summary

The Z-300 shows promise to solve an important material verification need within the food and pharmaceutical industries – specifically the analysis of ionically bonded salts that are insensitive to traditional molecular techniques Raman and NIR. The Z-300 combines a proprietary laser, on-board argon purge, and wide range spectrometer into a high performance handheld LIBS analyzer. These features – unique to the SciAps LIBS products – provide measurements of any group of elements in the periodic table. The novel sample detection system allows the device to be operated under Class 1 conditions, thus eliminating the regulatory requirements of x-ray and class 3b LIBS devices.

Z 300

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