

**ON THE SUITABILITY OF PORTABLE X-RAY FLUORESCENCE ANALYZERS
FOR RAPID SCREENING OF TOXIC ELEMENTS**

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ABSTRACT

X-Ray Fluorescence spectrometry (XRF) has been routinely used for alloy testing, determination of Pb in paint, and determination of Cd in plastic. However, its use to screen for toxic elements in food and medicinal products has been surprisingly limited to date. While XRF is less sensitive than atomic spectrometry methods such as ICP-AES and ICP-MS, it offers a number of significant advantages including minimal sample preparation, rapid analysis times, multi-element detection, and true field use using hand-held analyzers. The goal of this study was to evaluate the capabilities and limitations of two different portable XRF analyzers from Niton and Innov-X. The samples chosen for this study included liquid, semi-solid, and solid substances (cranberry juice, yogurt, and chocolate). Samples were fortified with up to four different toxic elements (arsenic, lead, mercury, and/or selenium) to give known concentrations on a weight-weight basis. Samples were analyzed via XRF and the resulting data were evaluated to ascertain figures of merit including selectivity, limits of detection (LODs), linear dynamic range, accuracy, precision, and speed. Selectivity was generally good and positive detection can be confirmed through the observation of multiple emission lines for an element. Although accurate quantitation of multiple elements may be compromised by overlap of emission lines, one would generally not expect to see the presence of several toxic elements in a given product. The sensitivity of the Innov-X analyzer was nearly an order of magnitude better than the Niton, with LODs in the 5-10 ppm range for all four target elements. Calibration curves were linear across more than three orders of magnitude spanning concentrations from the LOD out to percent levels. The accuracy of the Innov-X analyzer was slightly better than the Niton, with relative errors typically less than 20%, which is particularly remarkable considering that no external calibration procedures were employed and these results were obtained using the manufacturer's standard quantitation algorithms. Precisions were quite good as well, with percent relative standard deviations (%RSDs) of 5% or less. The most attractive features of XRF are its speed and simplicity, with minimal sample preparation required, analysis times as short as a minute or less, and estimated throughputs of approximately 60 samples per hour using a device that is hand-held and can be operated by a non-expert. Collectively, these capabilities make XRF a powerful tool for screening of toxic elements and rapidly responding to emergency situations that require identification and quantitation of toxic elements.

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INTRODUCTION

XRF has been widely used for applications such as monitoring metals in alloys, metals in soil, Pb in paint, and Cd in plastic. Anderson described specific FDA applications of handheld XRF analyzers, including its use for determining toxic elements in tableware.¹ A survey of various ACS, Wiley, and Science Direct on-line databases using the keywords “XRF” and “food” produced showed surprisingly few publications over the period of 1980 to the present. Some selected applications include its use for monitoring trace metals in milk and dairy products;²⁻⁴ K and Ca in tea;⁵ metals in oysters;⁶ metals in fruits, vegetables and grain products;⁷ Cr in FD&C Blue dye;⁸ trace elements in fruit juices;⁹ metals in oriental spices;¹⁰ and Fe, Cu, and Zn in food premixes.¹¹ With continuing evolution of XRF sources, detectors, and software and the relatively recent development of ever more powerful portable XRF analyzers, it is appropriate to take a closer look at this technology for FDA-related applications.

XRF is a high-energy physical process that is associated with the basic electronic structure of atoms. When an X-ray photon strikes an atom, it dislodges an electron from one of its inner orbitals, typically the K and L shells. To regain stability, an electron from one of the outer orbitals fills this vacancy and in the process, excess energy is released in the form of an X-ray photon. Since the quantum states of each atom's electrons are fairly unique, the *energy* of the emitted photon is characteristic of that element and independent of its chemical form. The *number* of photons detected at a given energy is proportional to the concentration of the element.

While laboratory-grade XRF instruments have been in use since the early 1960's, evolutionary developments in hardware and software over the past decade have dramatically facilitated the development of portable devices. Portable XRF analyzers have three basic components: an X-ray source, a detector, and a digital pulse processor. The source is typically a gamma ray emitting radioisotope (i.e., ⁵⁵Fe, ¹⁰⁹Cd, or ²⁴¹Am), although X-ray tubes are becoming more common in newer analyzers and provide significant advantages that will be reviewed later. It should be noted that an X-ray source can be used as a probe for eliciting a response from an element *only* if the source energy is greater than the absorption edge energy of that target element. The X-ray radiation strikes the target and the resulting X-ray fluorescence from the sample is collected by a thermoelectrically cooled solid-state detector. Most portable XRF analyzers are energy dispersive as opposed to wavelength dispersive, and a digital pulse processor monitors both the energy of the X-rays and the number arriving per unit time. Composition data (i.e., elements present, their relative concentrations, and uncertainties) are displayed in near real-time on the readout screen of the instrument. The analyzer is battery powered and can typically be operated for several hours without recharging. A photograph of one of the portable XRF analyzers used in this work is shown in Figure 1.

The goal of this study was to investigate the utility of field portable, energy-dispersive XRF for the determination of toxic elements in food products. Two different XRF analyzers (Niton and Innov-X) were used in the study of the detection of up to four different toxic metals (As, Hg, Pb, Se) in three different food products (cranberry juice, yogurt, and chocolate).



Figure 1. Photograph of Niton model Xli728 portable XRF analyzer.

EXPERIMENTAL

Reagents

The samples chosen for this study were intended to cover a range of phases from liquid (Northland's Traditional Cranberry Juice) to semi-solid (Trader Joe's French Village Nonfat Yogurt) to solid (Trader Joe's Pound Plus Milk Chocolate). Samples were used "as is" without further processing, with the exception of the chocolate, which was melted in a microwave oven to facilitate mixing and homogenization. The target metals for this study were selected from the standpoint of toxicity and included As, Hg, Pb, and Se. Known volumes of NIST-traceable stock solutions (GFS Chemicals) were pipetted into a beaker to give a known mass of metal (i.e., $10,000 \text{ ppm As} * 0.1 \text{ mL} = 1000 \text{ } \mu\text{g As}$). A known mass of the sample was then added to the beaker and the contents were mixed with a spatula. Approximately 10 g of the mixture was placed into a XRF sample cup, which was sealed with Mylar film and a retaining ring, and subsequently analyzed via XRF.

Equipment

The XRF analyzers used in this study were a Niton model Xli 728e unit equipped with a ^{109}Cd source and an Innov-X model Alpha unit equipped with an X-ray tube. Both analyzers were used in soil or bulk mode, but it should be noted that other modes such as thin sample mode and alloy mode can be employed for other applications. The sample cups were placed directly in front of the shutter of the analyzer (Mylar film side towards the instrument) and the measurement process initiated by pulling the sample trigger button. Experimental protocols were similar to those documented in EPA method 6200 for the determination of metals in soils and sediments¹²

and have been documented in the form of a *draft* standard operating procedure for the determination of toxic elements in food, supplements, and medicines.¹³ Analysis times ranged from 0.5 to 2 minutes and triplicate measurements were taken to evaluate precision. Results were available in two different forms: instrument readouts (element detected, mean concentration in ppm, and uncertainty) and raw spectra (instrument response versus energy). Raw spectra were downloaded from the analyzer into Excel for subsequent data analysis and interpretation.

Safety considerations

The use of X-rays and radioactive materials are governed by numerous state and federal regulations. Users should consult their safety officers and study applicable regulations for more details on these issues. When operated properly, typical exposures from an XRF analyzer are far less than typical background sources. Nevertheless, such equipment requires a license and analysts should follow the tenet of ALARA in their operation, meaning that their use should be such that human exposure to X-rays should be “as low as reasonably achievable”. It should be noted that radioisotope-based XRF analyzers must be stored under several levels of locks to prevent their use by unauthorized personnel, and transport of such analyzers via standard mail or passenger aircraft is not permitted. X-ray tube-based analyzers are exempt from some of these restrictions, and hence may be preferable for field applications.

RESULTS AND DISCUSSION

A better understanding of the strengths and limitations of analytical methods can be gained by evaluating figures of merit such as selectivity, sensitivity, linearity, accuracy, precision, speed, size, and cost. Each of these figures of merit are evaluated here within the context of determining the four different target metals (As, Hg, Pb, and Se) in three different matrices (cranberry juice, yogurt, and chocolate) using two different portable XRF analyzers.

First, a brief discussion of the theory and basic features of XRF spectra is appropriate. Figure 2 shows a partial energy level diagram for Pb that illustrates both excitation and emission. For this element, 88 keV photons are required to excite and remove K shell electrons and 16 keV photons are required for L shell electrons. The emission process can be initiated from several different energy levels. The notation used to differentiate between the various emission lines uses a letter (i.e., K or L) to refer to the shell that had the original vacancy, and a subscript (i.e., α or β) to denote the shell from which the vacancy was filled. For example, L_{α} corresponds to an M shell electron filling a vacancy in an L shell, and L_{β} refers to the N shell electron filling a vacancy in an L shell.

Figure 3 shows an XRF spectrum of 1% Pb in chocolate, which plots emission intensity measured in units of counts per second (cps) as a function of energy (keV). The three peaks around 20-25 keV are due to Compton backscattering of X-ray photons from the ^{109}Cd source. The three peaks at 10.5, 12.6, and 14.8 keV are due to Pb fluorescence from the sample corresponding to L_{α} , L_{β} , and L_{γ} transitions, respectively. Transitions from the next higher shell are more favored and hence L_{α} lines are usually more intense than L_{β} lines. This is not the case for the data shown in Figure 3, in which the L_{β} line is more intense due to more efficient re-absorption and scattering of lower energy L_{α} emission by the sample.

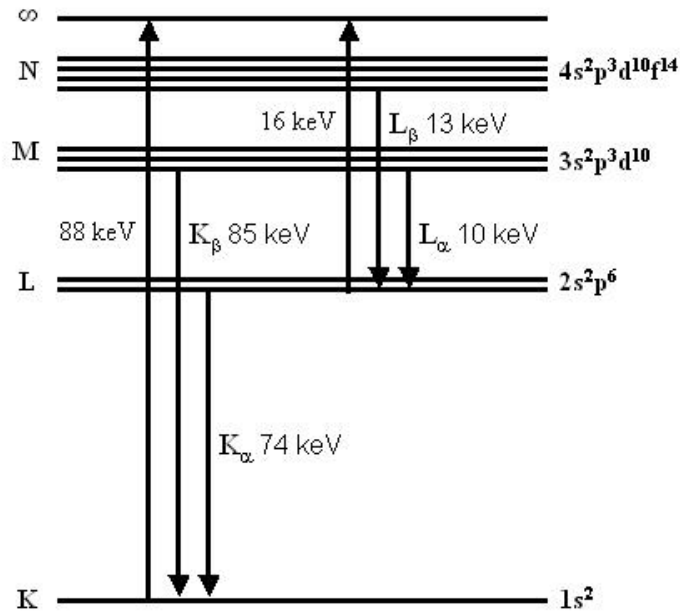


Figure 2. Energy level diagram showing excitation and emission energies for Pb.

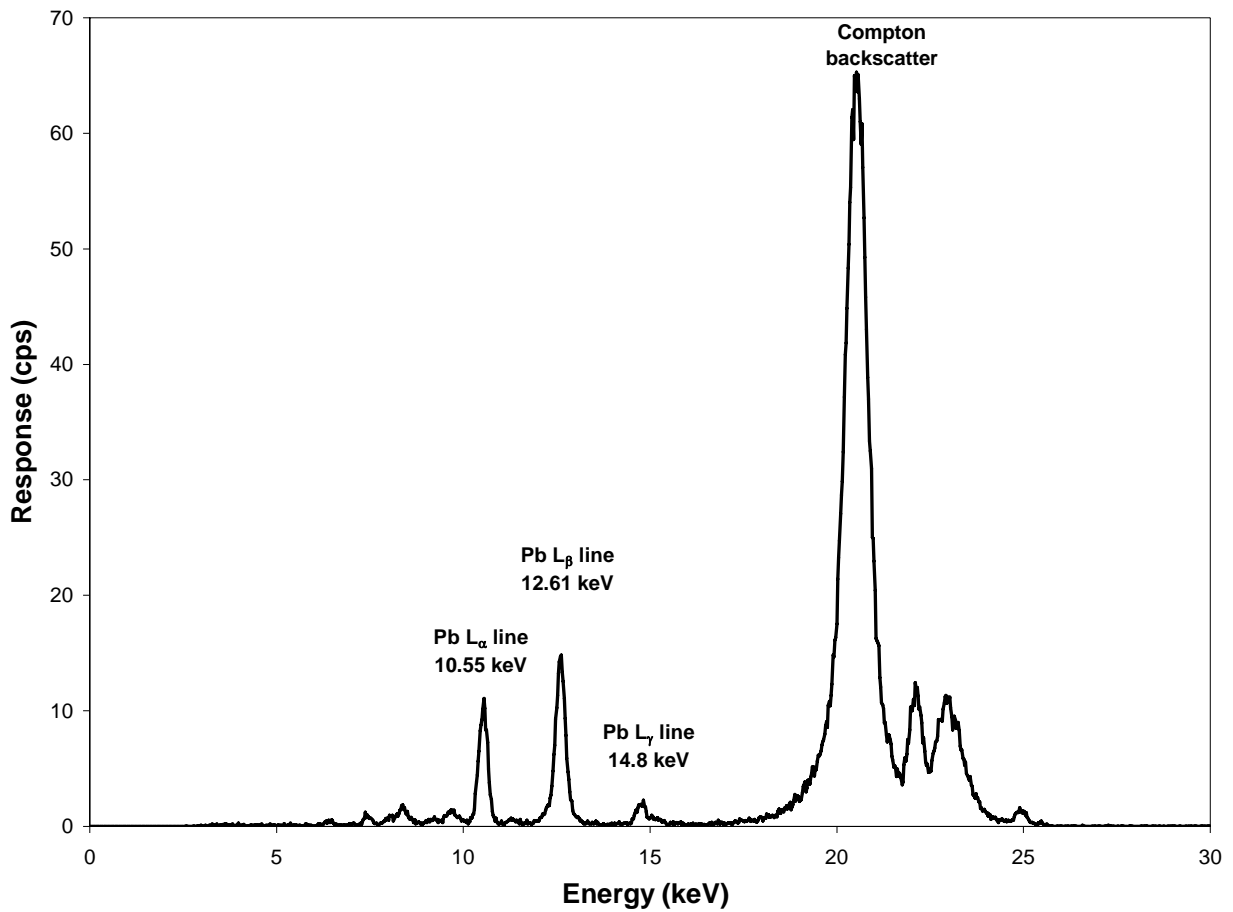


Figure 3. XRF spectrum of 1% Pb in chocolate.

Selectivity

XRF can be used to measure approximately 80 different elements in the periodic table ranging from Na to U. Selectivity is governed by factors such as resolution, overlap of emission lines, and the sample matrix. The Niton and Innov-X analyzers, both of which are equipped with thermoelectrically cooled detectors, have spectral resolutions of 0.5 and 0.2 keV measured as full width at half maximum (FWHM), respectively. Characteristic emission lines for each element are typically documented in the form of a list of corresponding energies for the K and L lines for each element.¹⁴ A subset of this information is presented in Table 1, which shows photon energies for the four target elements.

Table 1. Photon energies of principal K- and L-shell emission lines for the four target elements in units of keV. Potential interferences are shown in parentheses.

Element	K _α	K _β	L _α	L _β	L _γ
As	10.5 (Pb)	11.7 (Hg)	1.3	1.3	
Hg	70.2	80.7	10.0	11.8 (As)	13.8
Pb	74.2	85.4	10.5 (As)	12.6 (Se)	14.8
Se	11.2	12.5 (Pb)	1.4	1.4	

Confirmation of positive *detection* of an element would ideally require observation of *at least two* experimentally observed emission lines at energies that closely match the reference values for that element. Accurate *quantitation* of an element would ideally require the use of a *unique* emission line, which may not be possible for all target elements in a given sample matrix. A closer inspection of the data in Table 1 shows a number of potential interferences. To give two examples, emission at 10.5 keV could be due to either As (K_α) or Pb (L_α), and emission in the range of 11.7-11.8 keV could be due to either As (K_β) or Hg (L_β).

Given these overlapping emission lines, it was not possible to accurately determine As in the presence of significant levels of both Pb and Hg. Hence, accurate evaluation of the LODs for As required the preparation of separate standards containing only this element in the various matrices. The three other target elements could be determined simultaneously as they each gave a fairly unique emission line as shown in Figure 4. Here, Hg can be quantified using the L_α emission line at 10.0 keV and/or the L_β line at 11.8 keV, Pb using the L_α emission line at 10.5 keV, and Se using the L_α line at 11.2 keV. The additional line appearing at 12.5-12.6 keV is due to both Pb and Se. Given the potential for spectral interferences, users are advised to carefully choose emission lines to ensure both reliable detection and quantitation of the element(s) of interest for specific applications.

Sensitivity

The sensitivity of XRF depends on a number of factors, including the type and strength of the X-ray source, type and efficiency of the detector, measurement time, sample density, sample matrix, and target element. Figures 5 and 6 show XRF spectra of Pb in chocolate acquired using the Niton and Innov-X analyzers, respectively. Estimation of LODs was based on the use of data from three replicate spectra of a known concentration, where the signal-to-noise ratio

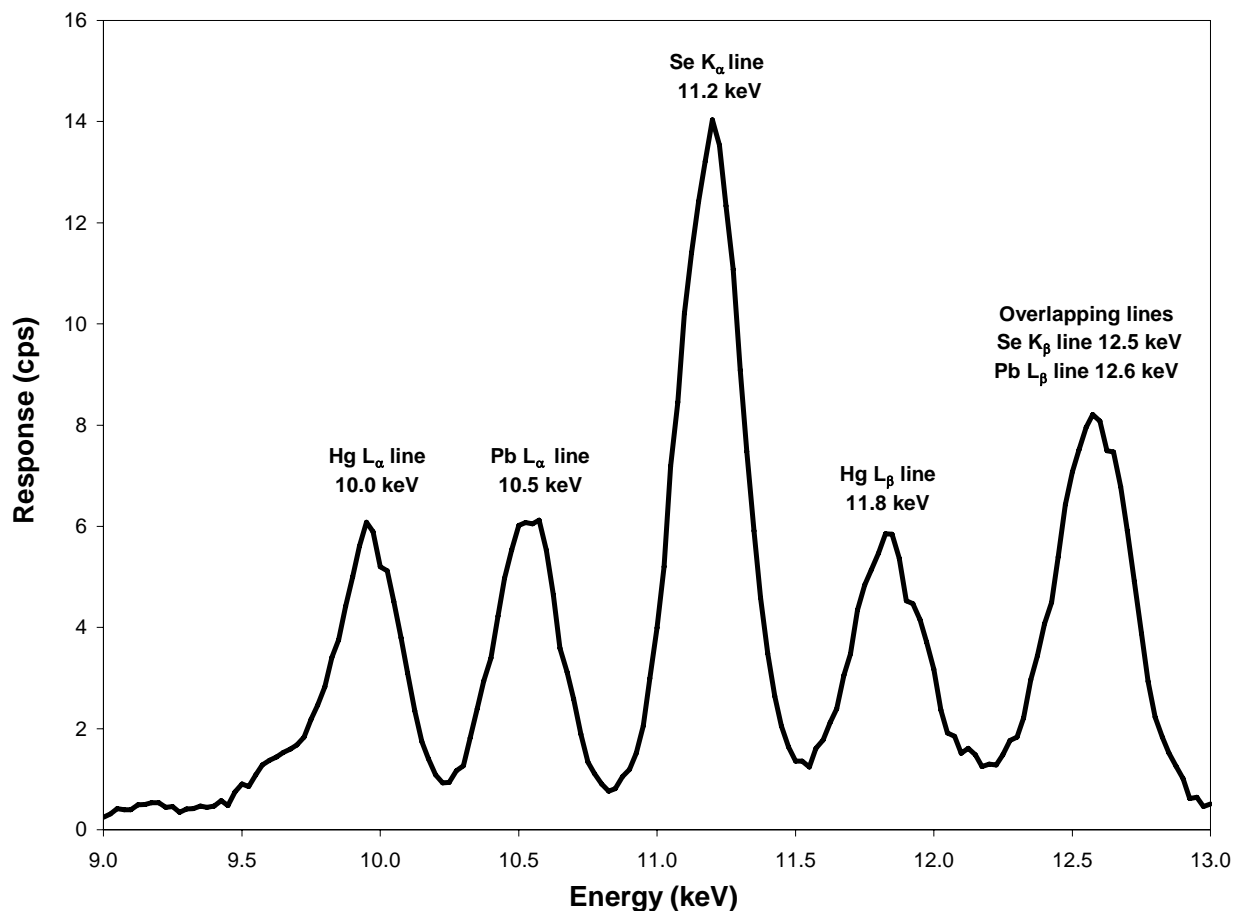


Figure 4. XRF spectra of 1000 ppm Hg, Pb, and Se in yogurt.

(S/N) was computed from the mean instrument response divided by the standard deviation of that response, and extrapolating this data to compute the concentration that would give S/N of 3. Comparison of the data in Figures 5 and 6 show that the Innov-X analyzer gave a signal magnitude approximately five times greater than the Niton analyzer for the 500 ppm standard and hence provides better S/N and lower LODs.

The studies were extended to determine LODs for various toxic elements in several different sample matrices. The results are shown in Table 2. LODs were fairly independent of the sample matrices, although LODs for Pb were three times higher in chocolate compared to cranberry juice and yogurt matrices (300 vs. 100 ppm). This may be due to the greater density of chocolate versus the other two matrices. LODs for Pb alone in the three sample matrices (100, 100, and 300 ppm) were not quite as low those obtained for Pb along with Hg and Se in yogurt (50 and 10 ppm). This can be attributed to the use of the different measurement times used in these studies (0.5 min vs. 2 min, respectively). Comparison of LODs for the four different elements showed minor differences, with Hg giving the poorest LODs (100 ppm in yogurt using the Niton analyzer) and Se giving the best LODs (5 ppm in yogurt using the Innov-X analyzer). LODs on the Innov-X analyzer were approximately a factor of five to ten times lower than the Niton analyzer. It should be noted that newer Niton analyzers may be more sensitive than the model used in this study.

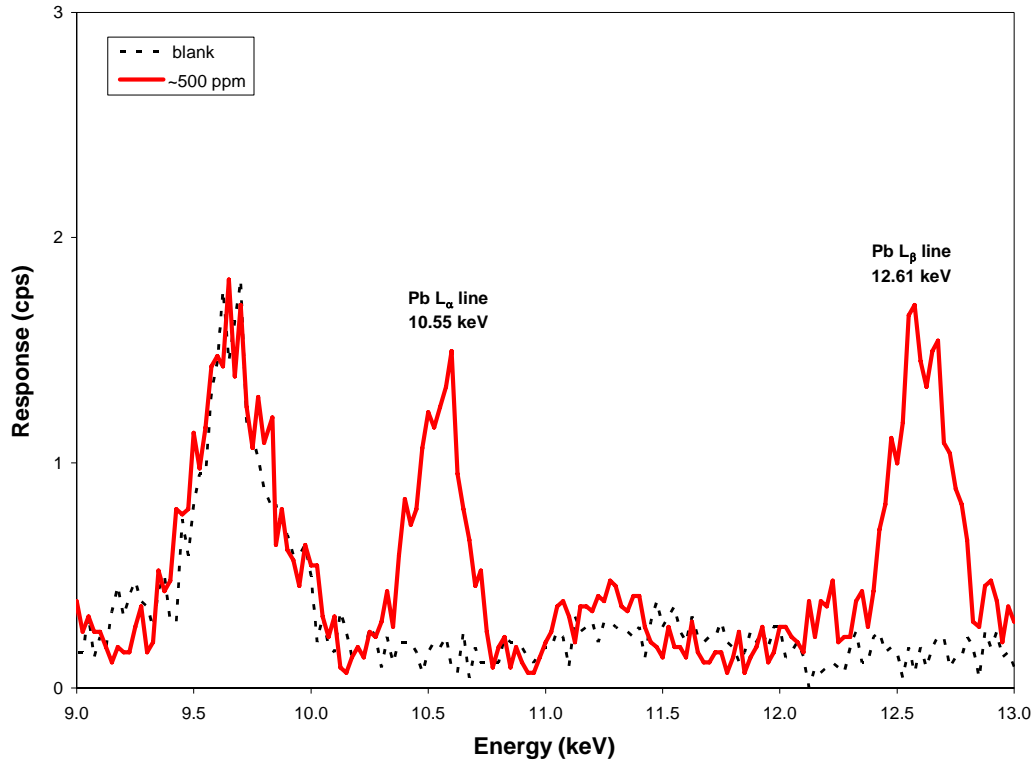


Figure 5. XRF spectra of Pb in chocolate acquired on Niton analyzer.

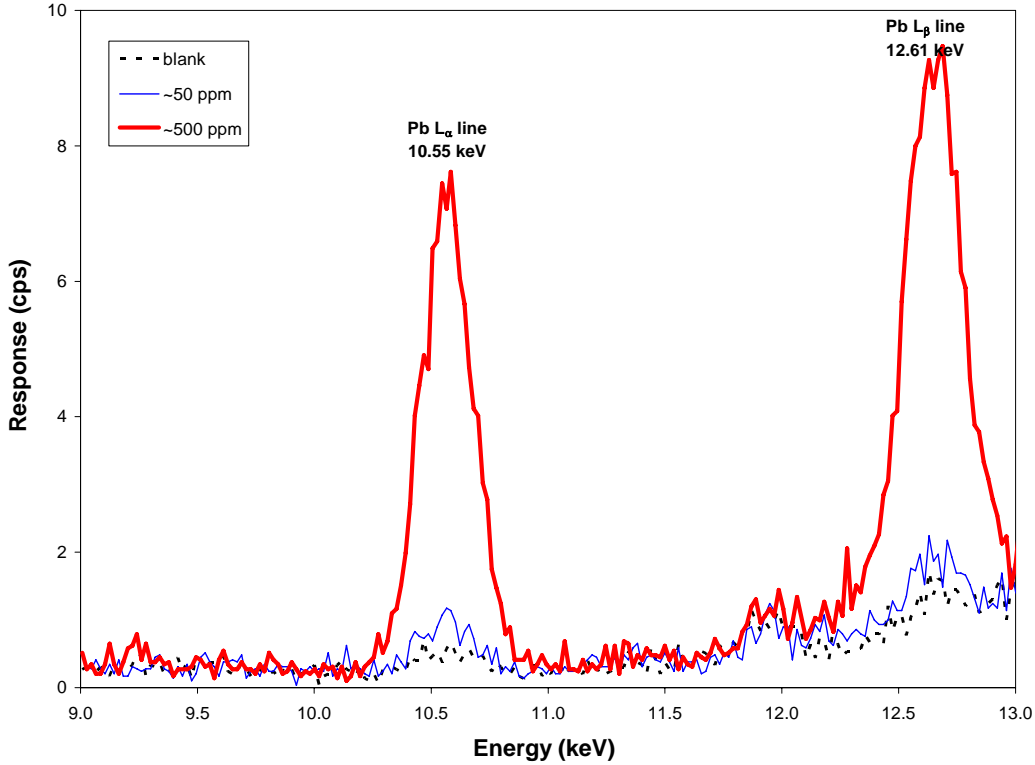


Figure 6. XRF spectra of Pb in chocolate acquired on Innov-X analyzer.

Table 2. LODs for various elements in several matrices. Time refers to measurement time and N/A denotes not applicable.

Analyte and matrix (analyzer, time)	As	Hg	Pb	Se
Pb in cranberry juice (Niton, 0.5 min)	N/A	N/A	100 ppm	N/A
Pb in yogurt (Niton, 0.5 min)	N/A	N/A	100 ppm	N/A
Pb in chocolate (Niton, 0.5 min)	N/A	N/A	300 ppm	N/A
As in yogurt (Niton, 2 min)	50 ppm	N/A	N/A	N/A
As in yogurt (Innov-X, 2 min)	10 ppm	N/A	N/A	N/A
Hg, Se, and Pb in yogurt (Niton, 2 min)	N/A	100 ppm	50 ppm	50 ppm
Hg, Se, and Pb in yogurt (Innov-X, 2 min)	N/A	10 ppm	10 ppm	5 ppm

Linearity

Linearity of instrument response was determined by analyzing several standards of various elements over a range of concentrations. Figure 7 shows representative calibration curves for As, Hg, Pb, and Se in yogurt obtained with the Innov-X analyzer. Similar results were obtained with the Niton analyzer.

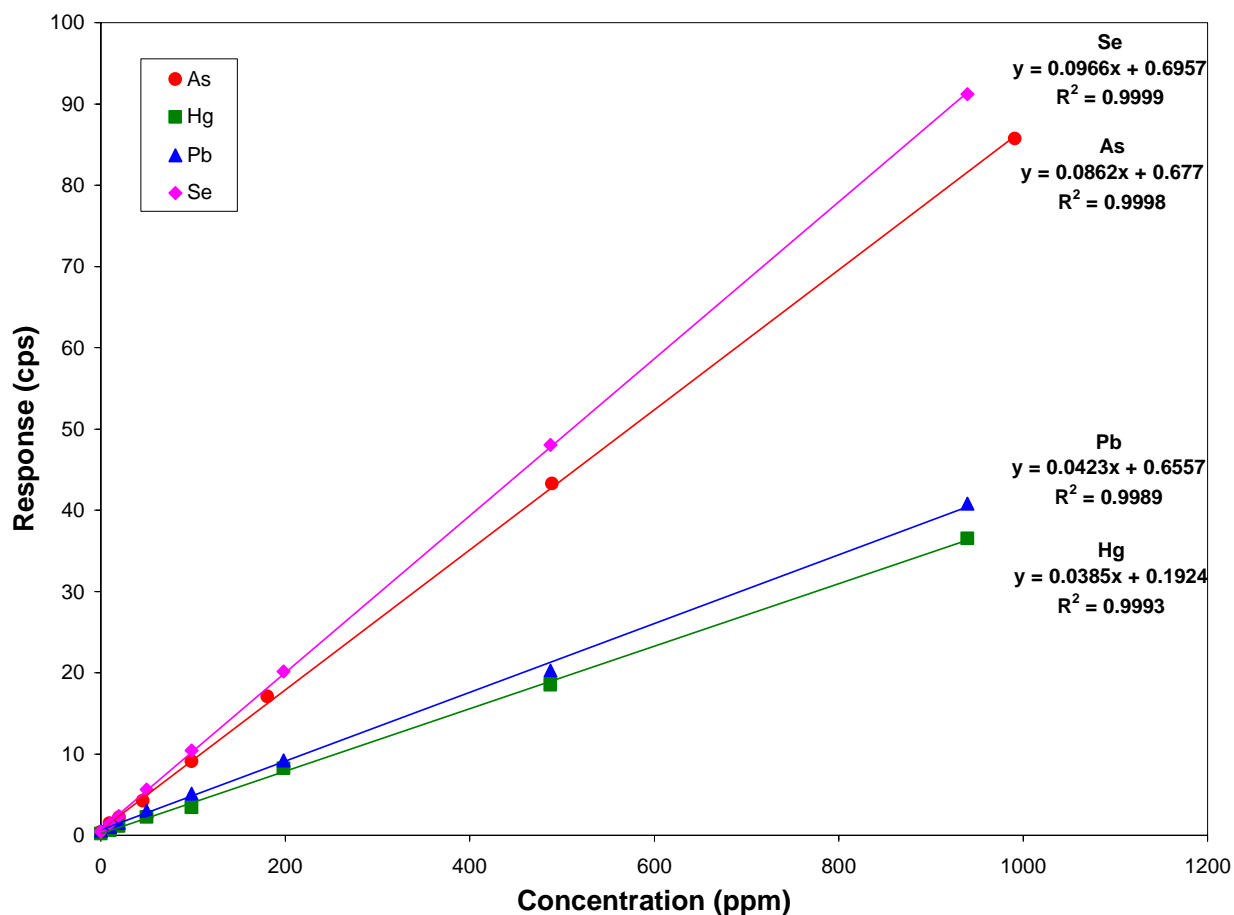


Figure 7. Calibration curves for As, Hg, Pb, and Se in yogurt using the Innov-X analyzer.

Y-axis values were computed from the mean of triplicate measurements of instrument response. The increased slopes of regression lines for Se and As versus Pb and Hg indicate better sensitivity for these elements, which corroborates the results shown in Table 2. The curves show excellent linearity with correlation coefficients (R^2 values) of 0.999 or better over a range of concentrations spanning almost two orders of magnitude from near the LOD at 10 ppm to the highest concentration of 1000 ppm. In separate studies, calibration curves were found to be linear out to concentrations as high as 10,000 ppm (1%) for all four elements.

Accuracy

Figure 8 shows plots of instrument readings (computed automatically via analyzer software) versus actual concentrations for determination of As, Hg, Pb, and Se in yogurt using the Innov-X analyzer. Again, similar results were obtained with the Niton analyzer. Ideally, these lines should have a slope of one, indicating perfect accuracy and one-to-one correlation between instrument readings and true concentrations. The slopes shown here are all greater than one, which leads to either positive or negative errors in instrument readings as shown in Table 3.

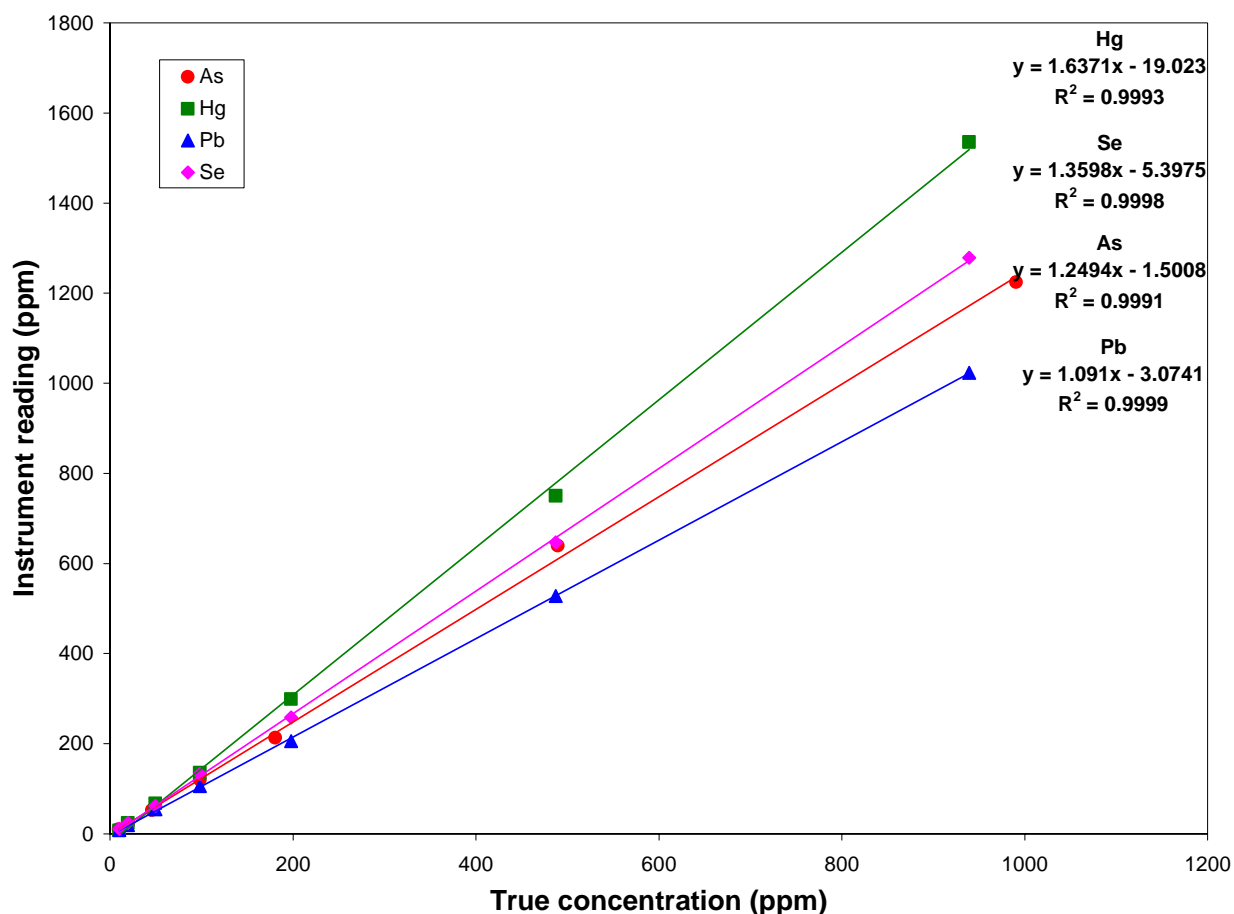


Figure 8. Accuracy curves for determination of As, Hg, Pb, and Se in yogurt using the Innov-X analyzer.

Table 3. Percent relative errors associated with instrument-computed concentrations of Pb in yogurt using two different XRF analyzers.

<u>Pb Concentration</u>	<u>Niton</u>	<u>Innov-X</u>
10 ppm	-23%	-13%
20 ppm	-13%	0%
50 ppm	-6%	8%
99 ppm	9%	7%
198 ppm	8%	4%
487 ppm	6%	8%
939 ppm	11%	9%

Relative errors were all less than 25% for Pb standards in the range of 10 to 1000 ppm for both the Niton and Innov-X analyzers. This is quite impressive considering that *no external standards were used to calibrate instrument response* in this study. The Innov-X analyzer appeared to give slightly better accuracy than the Niton analyzer, as evidenced by smaller relative errors for most of the standards analyzed. On the lower end of the calibration curves, relative errors were frequently negative. For example, analysis of a 50 ppm Pb in yogurt on the Niton analyzer gave a low reading of 47 ppm, corresponding to a relative error of -6%. At or near the LOD, these errors can lead to false negatives (experimental data indicating that the element was not detected when it was actually present). On the upper end of the calibration curves, relative errors were typically positive and may be even larger at higher concentrations.

The XRF analyzers and associated software estimate concentrations using instrument response at characteristic emission lines and Compton normalization to correct for sample density.^{12,14} In some cases, the software corrects for interferences due to overlapping emission lines, but the details of the algorithms used to do this were not provided. If one assumes that these algorithms give correct results for the application in question, this mode of operation provides one of the most advantageous features of XRF; that is, its use in the field for direct readout of elemental composition without prior calibration. For screening of toxic elements and/or contaminated samples, information on the elements present and their approximate concentrations based on such indirect quantitation may be acceptable. Applications that require more accurate quantitation necessitate the preparation of authentic standards in the matrices of interest, sample homogenization, and calibration of instrument response.

Precision

XRF spectra are acquired using an energy analyzer, in which X-ray photons at various energies are counted as a function of time. As a result, Fellget's (multiplex) advantage applies and S/N is proportional to the square root of measurement time.¹⁵ This is illustrated very nicely in Figure 9, which provides a plot of S/N as a function of measurement time on the Niton analyzer. Here, S/N was computed from the instrument reading divided by one half of instrument-reported uncertainty (which is equivalent to plus or minus two standard deviations¹⁴). The data were fitted to an exponential equation of the general form $y = kx^n$, which gave a correlation coefficient very close to one and an n value of 0.504. This is very close to the theoretical value of 1/2.

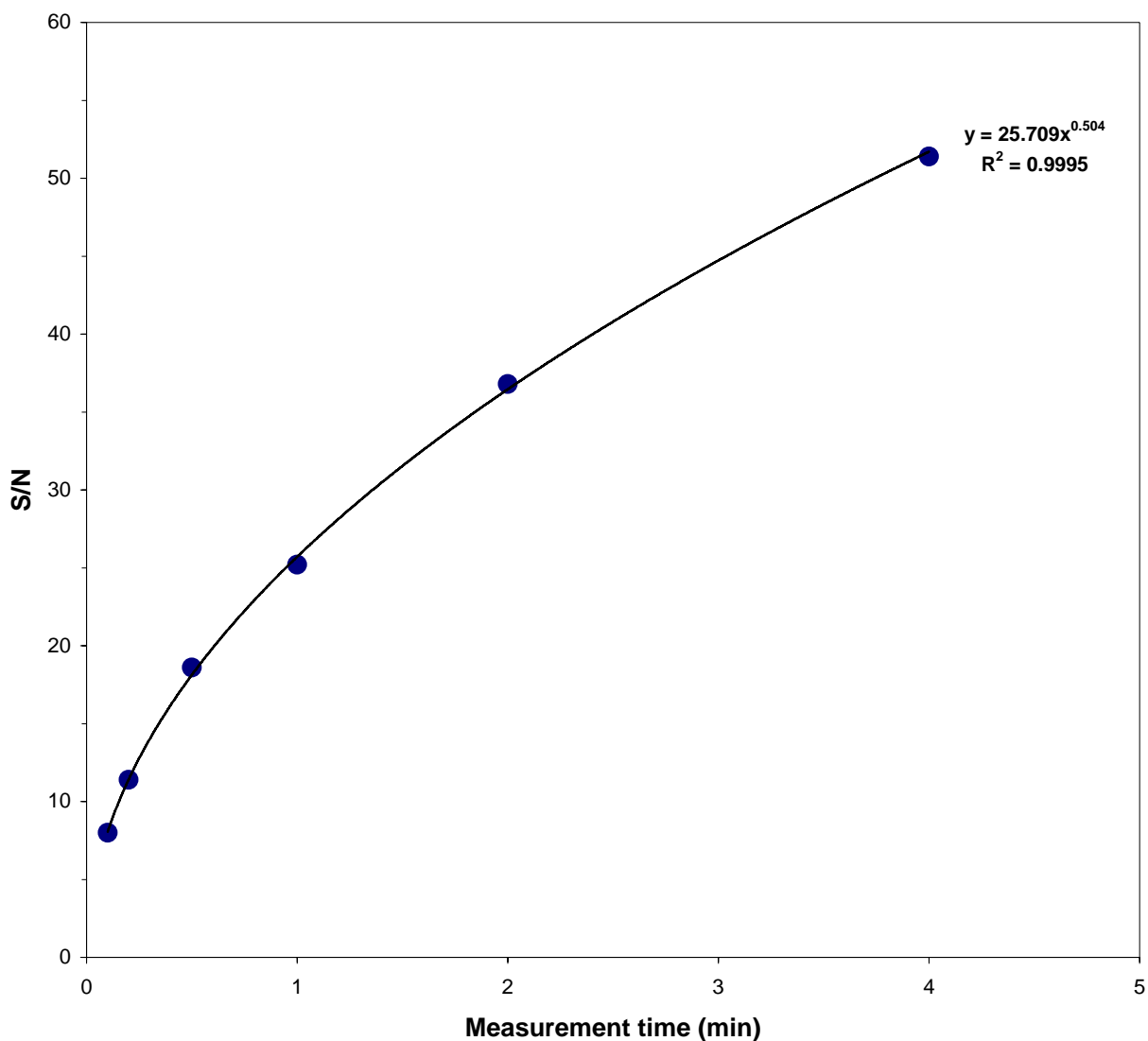


Figure 9. Signal-to-noise (S/N) as a function of measurement time in the analysis of 100 ppm Pb in yogurt using the Niton analyzer.

This figure clearly shows that improved S/N and hence better precision can be obtained at the expense of longer measurement times. When short measurement times are used, low counts give poor statistics and hence low S/N values. At very long measurement times, high counts provide better statistics and S/N values, but diminishing returns due to the square root relationship between S/N and time. It should be mentioned that the low %RSDs at longer measurement times can be misleading, as precision is *unrelated* to accuracy, and it is the accuracy of the determination which ultimately is the limiting factor here. A 1-2 minute measurement time is recommended to provide a good compromise between speed and precision. Using these measurement times, relative errors in both instrument readings and instrument responses above the LOD were typically less than 5% in all of these studies.

Speed

There are significant advantages associated with the minimal sample preparation requirements and nondestructive sampling capabilities of XRF. For ceramicware and tableware, semi-quantitative results can be obtained directly. For spices and supplements, semi-quantitative results can be obtained without the need for removing the sample from its package. For most typical field applications, samples are transferred to a sample cup and analyzed “as is” to facilitate rapid screening of toxic elements in large numbers of samples (i.e., supplements and medicines). For lab-based applications, better quantitative results can be obtained by homogenizing and/or grinding the sample prior to analysis. In all of these cases, the sample preparation procedures are far easier and faster compared to conventional atomic spectrometric methods that typically require digestion, extraction, filtration, and dilution. Moreover, the sample itself can be preserved for confirmatory analyses and future studies.

XRF also provides very fast analysis times. As mentioned above, a measurement time on the order of 1-2 minutes is more than adequate for identifying major and ppm-level constituents. Since authentic standards are typically not required for good quantitation, further time savings are realized. Here again, sample analysis via XRF is much easier and faster compared to conventional atomic spectrometric methods, and the simplicity and speed of this technique make it an ideal tool in screening large numbers of samples. Using a two-person team, one to prepare the samples and transfer them to cups and the other to take the measurements, it is not unreasonable to realize sample throughputs of up to 60 samples per hour. This is again far better than standard spectrometric methods, and it should be further noted that these analyses can be performed on-site at a factory or at a postal facility, which can greatly facilitate identification of potentially toxic products.

CONCLUSIONS

Energy dispersive XRF analyzers represent a powerful tool for a number of FDA applications. These analyzers are field portable, hand-held, and priced in the range of \$25,000 to \$35,000 depending on the manufacturer, model, and options desired. Given that different radioactive sources (i.e., ^{55}Fe , ^{109}Cd , ^{241}Am) may be required to measure a wide variety of target elements and the relatively short half-lives of some isotopes (i.e., 1.3 years for ^{109}Cd), the purchase of X-ray tube-based analyzers appear to be preferable over radioisotope-based analyzers due to fewer regulations associated with their use and lower frequency of replacement.

While other atomic spectrometry techniques may provide greater selectivity and sensitivity, XRF offers fairly selective detection of up to 80 different elements with LODs in the low ppm range. Compared to other atomic spectrometry techniques such as ICP-AES or ICP-MS, the most important advantages of XRF are simplicity and speed. XRF analyzers are operational within a few minutes after powering up, give direct readout of the elements present and their concentrations without the need for external calibration, and can be used by personnel with minimal training. The sample preparation and analysis procedures are fast, easy, and relatively straightforward. Samples can often be analyzed “as-is” for semi-quantitative data or homogenized and transferred to a sample cup for analysis if better quantitative data are desired. Sample analysis times are on the order of 1 to 2 minutes.

The most appropriate applications of XRF are those that take best advantage of its speed, small size, and nondestructive analysis capabilities. XRF can be used as a triage tool in the lab to investigate consumer complaints and potential food poisoning cases.¹⁶ It can also be used for homeland security applications associated with monitoring for the presence of the majority of the potentially toxic elements in the periodic table in foods, food ingredients, dietary supplements, and folk medicines. Its value as a triage tool can also be extended to expand the scope of analyses where initially only a single element determination was intended, and to exclude samples from analysis in the event of an emergency or crisis situation associated with a specifically identified toxic element. This latter capability tends to be greatly underappreciated until a lab is presented with hundreds of samples reflecting large numbers of product lots held from commerce pending analysis. It can also be used as a screening tool to provide information to prevent highly concentrated forms of an element from unknowingly entering the trace-level analytical process and causing significant disruption to sample workloads and the need for subsequent decontamination of glassware and equipment. More details on these applications will be reported in a forthcoming LIB.

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