Rapid and Accurate Determination of Iron in Vitamins and Supplements via XRF
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Sales of dietary supplements in the U.S. have increased from $19 billion to $25 billion between 2009 and 2013 [1]. While most of these products are deemed to be safe, a number of studies have reported on dietary supplements that are contaminated with heavy metals or are mislabeled with respect to the ingredients. Manufacturers are responsible for providing information on the levels of nutrients in these products. Chemical analysis, either by the manufacturer or an outside lab, is required to confirm that these products meet specifications. This is particularly important for iron, which has different Recommended Daily Allowances (RDAs) based on a person’s age, sex, and condition [2]. It should be noted that although iron is an essential nutrient, “iron overdose has been one of the leading causes of poisoning deaths in children younger than 6 years” [3]. Determination of iron in vitamins and supplements can be accomplished using UV/Vis Spectrophotometry, ICP-AES, ICP-MS, and other techniques. All of these methods require preparation of a homogeneous sample as well as dissolution, extraction, and/or digestion of the sample prior to analysis. Because of this labor intensive step, the analysis process usually takes longer. This presentation describes the development, evaluation, and application of methods based on the use of handheld and lab-grade XRF instruments to accurately quantify iron in vitamins and supplements.

Three key features of this method are the use of a minimum of at least 20 pills or tablets to get a more representative sample, dilution of samples into cellulose to minimize matrix effects, and accurate determination of iron via XRF using custom standards for quantification. Even a vitamin SRM from NIST is not homogeneous and the certificate of analysis notes the following: “Individual tablets should not be analyzed because of tablet-to-tablet variability. The variation of measured element (concentrations) from tablet-to-tablet ranges from approximately 15-25%” [4]. In this work, pills were homogenized and mixed with cellulose using either a coffee grinder or a high speed tablet mill, with the latter giving better results. Accurate quantification can be problematic due to the wide variety of sample compositions and matrices, inter-element effects such as absorption or enhancement of fluorescence by other elements, and the lack of available standards for calibration. Although iron standards can be readily prepared by gravimetric dilution of known masses of iron into known masses of a diluent, it should be obvious that there is no single diluent that would match the wide variety of samples of interest. In situations such as this, either the samples must be diluted to the point at which matrix effects become negligible or the method of standard additions must be used. For this work, dilution factors of about 30 were large enough to reduce these matrix effects. XRF response was calibrated using standards ranging from 50 to 2000 ppm iron, which were prepared by mixing known masses of iron oxide and cellulose. Samples and standards were placed into cups and analyzed using an Olympus Delta handheld XRF analyzer and a Thermo Quant’X lab-grade XRF instrument using one minute measurement times. Calibration curves showed excellent linearity and demonstrated the viability of the method used to prepare standards. The accuracy of this method is demonstrated by the analysis of the NIST vitamin SRM, which gave relative errors of less than 5%. Precision of the method was good, with RSDs around 5% or less for samples and standards. Use of this method to determine iron levels in several different vitamin and supplement products showed some interesting results. Iron levels varied by as much as 30% from pill to pill, reinforcing the importance of prepared a homogeneous sample for analysis. A men’s vitamin product whose label indicated that it contained no iron was found to contain ~200 ppm iron. Several generic products were found to have iron concentrations that were outside the expected tolerance of 20% of the value indicated on the product label. Surprisingly, the performance of the handheld XRF analyzer was similar to the lab-grade instrument, is simple to use, and can be equipped with an algorithm that automatically computes concentrations of samples. The lab grade instrument requires more expertise to set up and define the method, but automates the analysis and generates a report.

Whether using a handheld or lab-grade XRF, these methods are deemed to be superior to conventional atomic spectrometry techniques as they do not require sample digestion, and are simpler, cheaper, and much faster. Ultimately, this method may find use in a regulatory setting to rapidly assess the levels of nutritional elements (iron, calcium), potentially toxic elements (selenium, lead), and catalytic elements in drugs and supplements.