

Status: Final

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Standard Operating Procedure for Screening Phosphorus, Chlorine, Bromine and Antimony in Consumer Products by X-Ray Fluorescence Spectrometry (XRF)s

1. SCOPE AND APPLICABILITY

This standard operating procedure (SOP) describes the technical steps and procedures for instrument operation and analysis of phosphorus, chlorine, bromine and antimony in solid samples (furnishing materials) using the ARL QUANT'X EDXRF Analyzer.

This SOP is based on but also represents a deviation from EPA method 6200. Method 6200 is applicable to the in situ and intrusive analysis of the 26 analytes for soil and sediment samples that can be detected by field portable x-ray fluorescence (FPXRF). This SOP describes the application of non-portable ARL QUANT'X EDXRF Analyzer as a pre-screening tool for phosphorus, chlorine, bromine and antimony in furnishing materials.

2. DEFINITIONS

- EDXRF – Energy Dispersion X-Ray Fluorescence Spectrometry
- ARL QUANT'X EDXRF – XRF Analyzer by Thermo Scientific
- ROI – Region of Interest
- SRM – Standard Reference Material
- eV – Electron Volt
- SDS – Safety Data Sheet
- REM – Roentgen Equivalent Man
- TLD – Thermal Luminescent Detector
- ARF – Authorization Request Form
- SAR – Sample Analysis Request

3. PRINCIPLE

The XRF technology described in this method uses a rhodium x-ray tube to irradiate samples with x-rays in 4-50 kV range. When a sample is irradiated with x-rays, the source x-rays may undergo

either scattering or absorption by the sample. When elements within the sample absorb the source x-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and therefore the outer shell electrons emit energy as they fill the inner shell vacancies. This rearrangement of electrons results in emission of x-rays characteristic of the element. The fluorescent radiation is analyzed by sorting the energies of the photons (EDXRF). Once sorted, the intensity of each characteristic radiation is directly related to the elemental composition of the sample.

4. INTERFERENCES

The total method error for XRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in XRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are discussed below.

- Matrix effects may result from variations in the physical character of the sample. These variations may include such parameters as particle size, homogeneity, density and surface condition. For heterogeneous consumer product samples, multiple scans at different locations can be averaged.
- Inconsistent positioning of the sample in front of the probe window is a potential source of error because the signal intensity decreases as the distance from the radioactive source increases. This error is minimized by maintaining a fixed distance between the x-ray window and each sample. For optimal results, the sampling surface should be smooth and positioned level with the x-ray window.
- Chemical matrix effects result from the presences of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as x-ray absorption and enhancement and may occur if heavy metals are present within the material.
- X-ray lines from different elements can be very close in energy and, therefore, can cause interference by producing an overlapped spectrum. The degree to which a detector can resolve the two different peaks depends on the energy resolution of the detector. If the energy difference between the two peaks in electron volts is less than the resolution of the detector in electron volts, then the detector will not be able to fully resolve the peaks. The most common spectrum overlaps involve the $K\beta$ line of element Z-1 with the $K\alpha$ line of element Z. This is called the $K\alpha/K\beta$ interference. Because the $K\alpha/K\beta$ intensity ratio for a given element usually is about 7:1, the interfering element, Z-1, must be present at large concentrations to cause a problem. The effects can be completely or partially corrected mathematically (through the use of deconvolution techniques) in UniQuant EDXRF Software. Other interferences can arise from K/L, K/M, and L/M line overlaps, although these overlaps are less common. As an example, chlorine detection can be compromised by sulfur (S $K\alpha$) and argon (Ar $L\alpha$) peaks, if the sample has a high sulfur content and or if the analysis is performed without vacuum or nitrogen/helium purging of the analyzer chamber (See Figure 1).
- Laboratory entrance sticky mats shall be used and changed daily to prevent contamination of the laboratory (tracking small particulates into the lab).

- Laboratory gloves shall be replaced after handling a sample to prevent sample cross contamination. The interior surface of the XRF shall be wiped with a low lint laboratory grade tissue if a sample is placed directly on the surface of the XRF analysis window. Wet laboratory tissue with deionized water to aid in removing small particles or fibers.

5. PRESERVATION AND HOLDING TIMES

5.1. Sample Containers

Consumer product samples are stored in sealed glass jars or sealed plastic bags fully enclosed in aluminum foil at room temperature or below. Single use aluminum foil or plastic bags can be used without prewash.

5.2. Preservation and Holding Times

Analysis should not exceed a 28-day maximum holding time. The holding time can be increased if the samples are stored in sealed containers and at a temperature of $< 5\text{ C}$.

Consumer products samples are subjected to a short sub-atmospheric vacuum environment when analyzed by XRF and therefore a potential loss of semi-volatile organics substances may occur. Repeated analysis of the same subsample should be limited and or monitored for decrease in signal intensity.

6. EQUIPMENT AND SETUP

6.1. Equipment

- ARL QUANT'X EDXRF Analyzer, PN #410408 (Thermo Scientific, USA)
- Vacuum Pump Edwards RV8, PN #10948779 (Edwards, Czech Republic)

6.2. Consumables

The recommended consumables are shown in Table 2. This list of consumables is a suggestion only, similar items can be used, however, precautions shall be made regarding possible interferences and materials compatibility.

7. STANDARDS AND REAGENTS USED

- Copper check standard (metallic Cu plate) for energy adjustments, OFHC by Thermo Scientific
- Calibration standards (See Table 1)

8. METHOD PROCEDURE

8.1. Batch QC Requirements

There are no specific batch requirements for screening of consumer products for phosphorus, chlorine, bromine and or antimony. However, it is recommended that a method blank is analyzed prior to the analysis of samples and after the detection of high levels of phosphorus, chlorine, bromine and or antimony. If carry over is suspected a method blank shall confirm instrument cleanness. It is also recommended to analyze a selected sample in duplicate to confirm sample handling and instrument precision.

8.2. Instrument QC requirements

EDXRF instrument should undergo a daily energy adjustment before sample analysis or calibration of instrument begins.

Initial Calibration: 3 or 5-point calibration curves are obtained for P, Cl, Br and Sb. A linear fit is used (Table 1 and Figure 2-5).

8.3. Sample Preparation

- (1) Most consumer product samples can be analyzed by placing the sample directly over the x-ray window. Samples such as plumage, polyester fibers, shredded foam and or other mixed materials will need to be placed in a sample cup sealed with a membrane film. Pack sample cells completely to minimize voids.
- (2) Large samples of dense foams shall be analyzed directly and heterogeneous foams averaged through several points.

8.4. Sample Analysis

8.4.1. Energy Adjustment of EDXRF

- (1) Power on instrument and ensure the x-ray safety key on rear of instrument is in the on position.
- (2) Access the lap top computer with user name "Thermo Scientific" and password "analyst".
- (3) Open sample chamber door and place copper plate (OFHC by Thermo Scientific) over XRF detector window. Ensure that the window aperture is completely covered by the copper plate.
- (4) Open "Acquisition Manager" software and navigate to File New Qualitative Tray List.
- (5) On the Qualitative Tray List (QTL) window navigate to Analyze Energy Adjustment.
- (6) Select "OK" on the Start Energy Adjustment window with the preset settings.
- (7) When the message "Energy Adjustment Has Completed." appears, select "OK". Then navigate to File Save Report... Reports are located in the C:\Quant'x\Reports\ folder. Use "Energy Adj Month Day Year" file name format and save Energy Adjustment Report.

8.4.2. Sample Set-up and Analysis

- (1) Before the analysis of samples, wipe the interior surface of the XRF with a lint free laboratory grade tissue lightly wetted with deionized water to remove any small fibers or other material and ensure surface is dry.

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- (2) Place sample in XRF analysis chamber and position sample (in a cup or directly in case of foams/fabrics) over the XRF detector window. It is recommended to subsample the consumer product samples.
- (3) Navigate to File New Quantitative Tray List.
- (4) Enter ECL or other identifying sample name in the sample field and load method "Furnishings P Cl Br Sb Mar 2016" located at C:\Quant\x\Methods\ in method field, methods are created from a template with calibration performed once every 1-2 years. All scans and sample analysis reports are stored in the method file.
- (5) To start the analysis, move the cursor to the next sequence line field and wait for method to load. Start analysis by selecting "Go".
- (6) Once the sample analysis is complete, check the position of any small fabric or foam samples to ensure the sample did not move off x-ray window during evacuation or pressurization of analysis chamber.
- (7) Print EDXRF Analysis Report page after all 4 scans are complete. Analysis reports can be located by sample name and opened from "Method Explorer". Sample analysis results are saved for each sample by saving the method in the "Method Explorer" window.
- (8) From the "Method Explorer" window navigate to "Method Tree" and expand the spectra folder.
- (9) Locate the analyzed samples and open each XRF scan one at a time (High Zb, Low Za, Low Zb and Mid Zc). Select the "Identify Spectrum Peaks" (red fingerprint icon) to identify and label the peaks by element name.
- (10) Select "Toggle KLM Markers" (KLM icon) and press Ctrl + left or right arrow to see element's characteristic XRF patterns.
- (11) For subsequent sample analysis, return to the "Acquisition Manager-MTL" window and select the "View Sample List" icon. Enter identifying sample name and proceed with analysis as is described above. Use unique sample names such as "AY00777a", "AY00777b" etc. if multiple scans are performed on a sample.

8.4.3. Method Creation and Calibration

- (1) Open "Method Explorer" and navigate to Method Tree and expand spectra folder.
- (2) Navigate to "Elemental Peak Profiles" in the tree on the left side of the screen
- (3) Open tab "Spectrum" and choose "Import"
- (4) Select the file for an element being added to the calibration for the correct filter, voltage, and count rate conditions e.g. "Cl K Series 8 kV Cellulose Reference low rate"
- (5) Repeat above steps for all elements and all conditions being added.

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- (6) Navigate to “Analytes and Conditions” on the left side of the screen. Remove Mid Zb row from the bottom with the left click and “Delete”
- (7) Open tab “Conditions” and choose “Add”
- (8) Choose the following conditions: Low Za, Low Zb, Mid Zc and High Zb.
- (9) Select P and Cl for Low Za, Cl and P for Low Zb, Br for Mid Zc and Sb for High Zb respectfully.
- (10) Then navigate to “Calibration” field on the left and enter standards information as is provided in Table 1. Also, files from C:\Quant’x\Standards\ can be opened by choosing “Calibration” “Add Standard”.
- (11) Save the method by clicking “File” “Save as”.
- (12) Then select “Calibration” tab on top and choose “Calibrate”, replace one standard after another when requested by “Method Explorer” program.
- (13) Save method again once all the scans are complete.

8.5. Data Analysis

- (3) Calculated phosphorus, chlorine, bromine and antimony concentrations are reported on each sample Analysis Report Page. A Not Detected result is indicated by “ND”, trace amount detected by “+” and major constituent as “++” on the Laboratory Report for Elemental Screening by XRF.
- (4) Print all 4 ROIs of the XRF spectra:
 - Low Za (No Filter, 4 kV, vacuum, low count rate, 100 sec) for P and Cl
 - Low Zb (Cellulose, 8 kV, vacuum, low count rate, 100 sec) for P and Cl
 - Mid Zc (Pd Thick, 28 kV, air, medium count rate, 100 sec) for Br
 - High Zb (Cu Thick, 50 kV, air, high count rate, 100 sec) for Sb

8.6. Data Reporting

A complete report packet shall include:

- (1) Laboratory Report for Elemental Screening by XRF.
- (2) Printout of the Analysis Report Page and 4 ROIs of the XRF spectra.
- (3) A copy of the Authorization Request Form (ARF).
- (4) A copy of the Sample Analysis Request (SAR).

- (5) A copy of all related sample receipt and chain-of-custody documentation, including any photographs taken upon sample receipt.
- (6) A copy of the certificates for all standards used in the analysis.
- (7) Any other notes collected during sample preparation or analysis.

8.7. Method Performance

Current method performance reports can be found on file with the Quality Assurance/Quality Control Officer.

9. MAINTENANCE AND TROUBLE SHOOTING

Maintenance required on an as-needed basis, such as changing mechanical pump oil, cleaning XRF air intake screens and testing the interlock circuit. Record maintenance performed in the XRF maintenance log book.

See Chapter 8 “Periodic Maintenance” of Quantx Technical Manual (Ref. 11.4).

10. REFERENCES

- 10.1. United States Environmental Protection Agency, “Method 6200 – Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment”, SW-846, Revision 0, February 2007.
<http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/6200.pdf> (Accessed on June 8th, 2015)
- 10.2. United States Environmental Protection Agency, “Inorganic Analysis, Chapter One”, SW-846, Revision 4, February 2007.
<http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/chap1.pdf> (Accessed on June 8th, 2015)
- 10.3. United States Environmental Protection Agency, “Inorganic Analysis, Chapter Three”, SW-846, Revision 4, February 2007.
<http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/chap3.pdf> (Accessed on June 8th, 2015)
- 10.4. Quantx Technical Manual. Thermo Scientific
- 10.5. WinTrace User’s Guide version 4.0. Thermo Scientific

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11. TABLES

Table 1. Calibration Standards

Standard	P %, Low Za	Cl %, Low Zb	Br %, Mid Zc	Sb ₂ O ₃ ppm, High Zb
P (elemental)	26.93	-	-	-
NIST 2709	0.062	-	-	9.457
NIST 2711	0.086	-	-	23.22
BR ROHS 1-3	-	0	0	10000
BR ROHS 2-3	-	0.5	0.1	10000
BR ROHS 3-3	-	1	0.5	15000

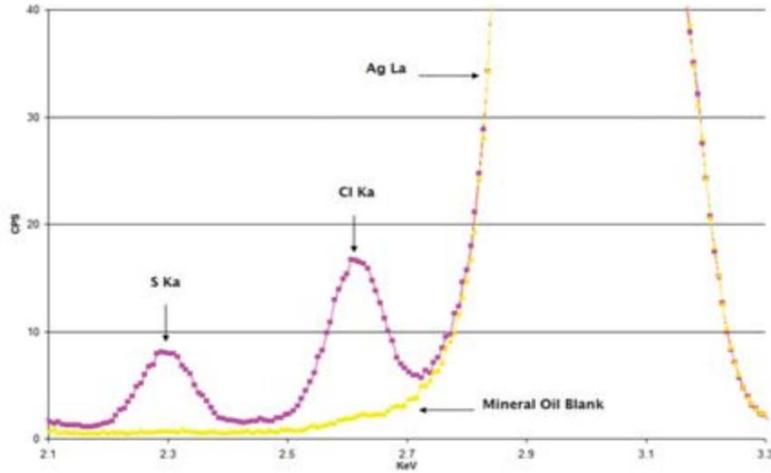
Table 2. Supplies and consumables

Name	Description	Supplier	PN #
Plastic XRF sample cups with closure rings	31mm diameter, 23mm height	Chemplex Cat, USA	1530
High Performance XRF Sample film	POLY 4 100m at 4 µm	Oxford Instruments, UK	L73
Oil mist filter	EMF10	Edwards, UK	A46226000
Roughing pump oil	Ultra Grade 19	Edwards, Canada	H11025015
Razor blades	Bi-Metal Heavy-duty	Irwin, USA	
Kimtech Kimwipes	37x42cm	Kimberly-Clark, Canada	
Extra Heavy Duty Aluminum Foil	18"x1000ft	Boardwalk, USA	BWK7136
XRF sample cell	32 mm	Premier Lab Supply, USA	SC-4331
Prolene Thin-Film	SpectroMembrane, 4µm	Chemplex Industries Inc., USA	
Deionized Water			

Note: these are suggested supplies and consumables

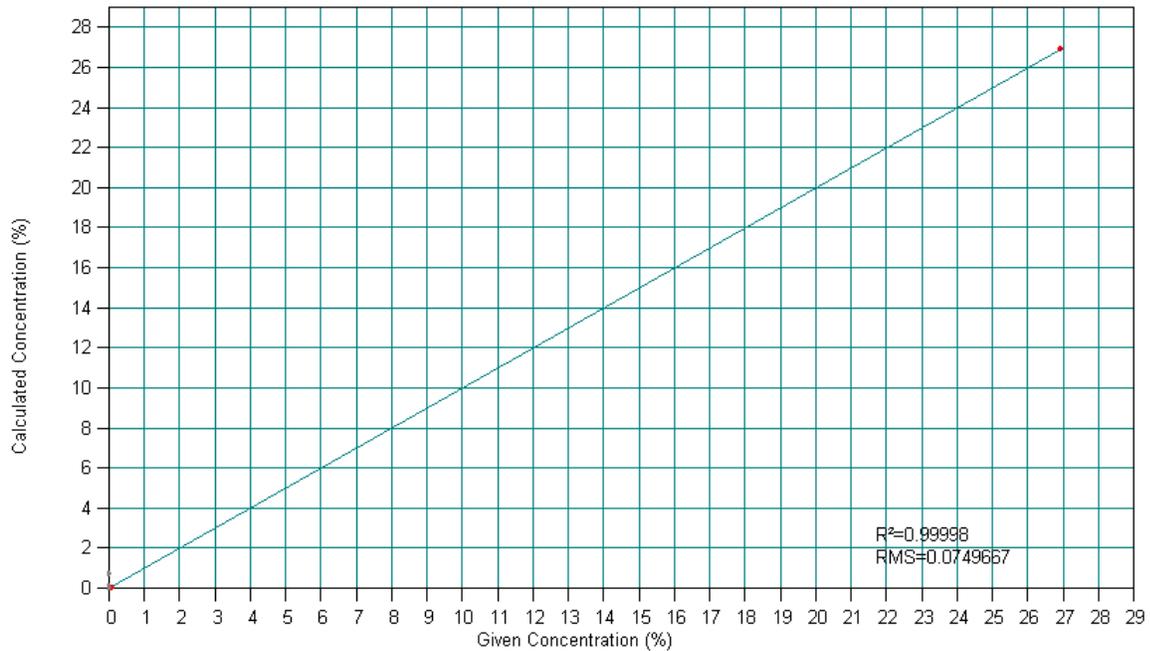
12. FIGURES

Figure 1



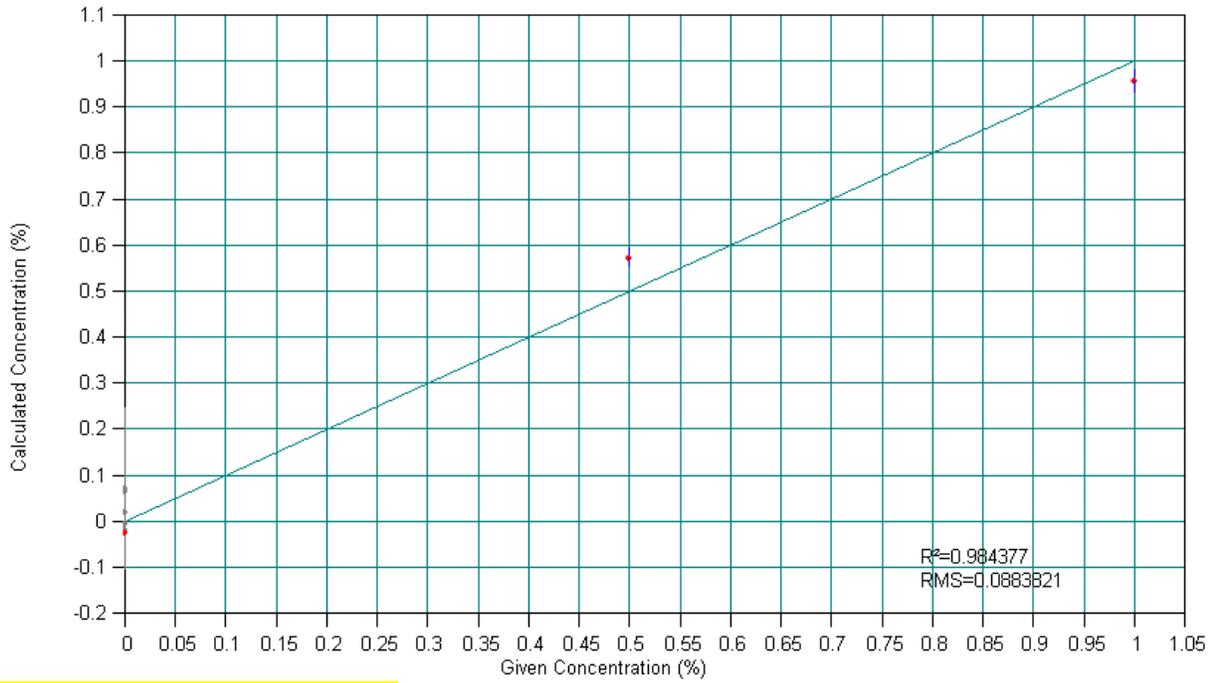
XRF spectra exhibiting atmospheric Argon interference.

Figure 2



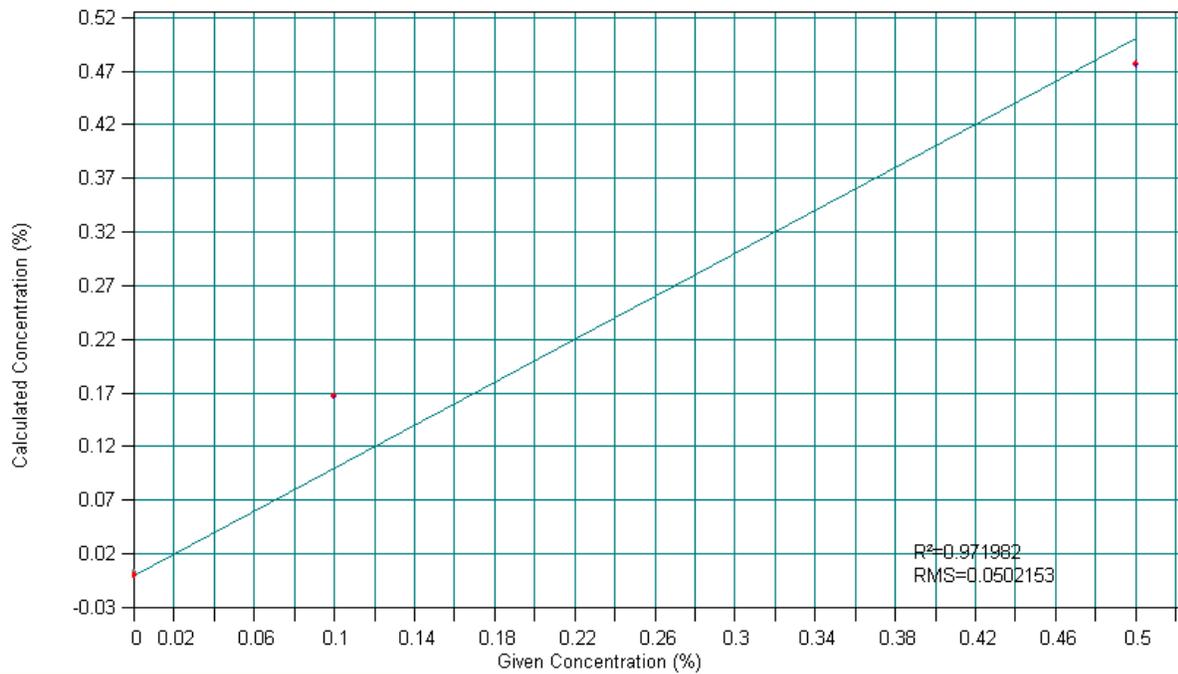
Phosphorus 3-point calibration curve.

Figure 3



Chlorine 3-point calibration curve.

Figure 4



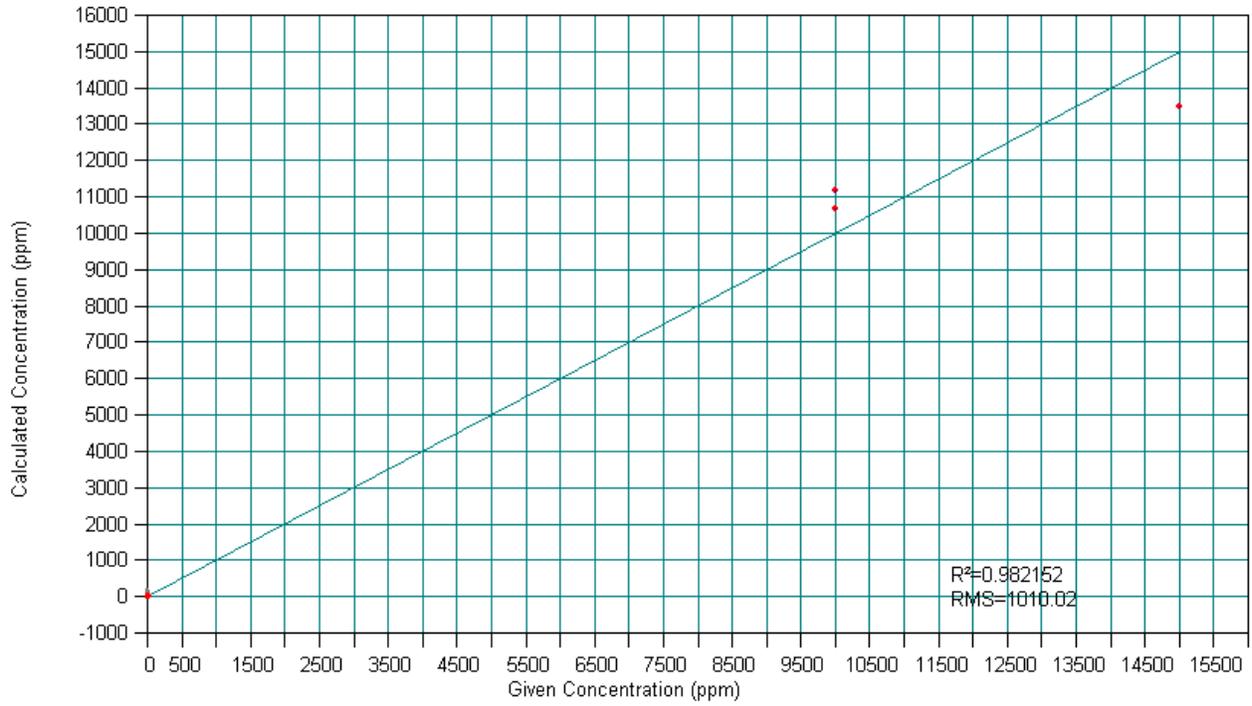
Bromine 3-point calibration curve.

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Figure 5



Antimony 5-point calibration curve.

