

Operation of the Bruker M4 Tornado X-Ray Fluorescence Spectrometer

1 Introduction

The Bruker M4 Tornado is an energy dispersive x-ray fluorescence spectrometer with fine focus and microspot analytical capabilities. These techniques are used for the analysis of samples that are too small for bulk x-ray fluorescence analysis methods.

2 Scope

This document applies to personnel using the associated instrument(s)/equipment in the following disciplines/categories of testing: general physical and chemical analysis in support of metallurgy, anthropology or general chemistry examinations. The operation of the Bruker M4 Tornado will follow the procedures outlined in the current revision of Chemistry Unit (CU) Metallurgy standard operating procedure (SOP) *Compositional Analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF)* and the specific parameters described below.

3 Principle

The Bruker M4 Tornado has two excitation options to generate the incident x-ray beam:

- 1) a rhodium target, microfocus x-ray tube (50 kV, 30W max) with a polycapillary lens delivering a 25 μm spot (micro-XRF), or
- 2) a molybdenum target, fine focus x-ray tube (50 kV, 40W max) with a 1.0 mm fixed collimator (collimated XRF).

A silicon drift detector (SDD) measures photons emitted by the sample. These components are arranged in a top-down configuration, with a working distance of approximately 10 mm. Specimens are placed face up on an adjustable stage for measurement. Elements with atomic number equal to and greater than 11 (sodium) can be measured. Measurements can be made in air or under vacuum.

Video cameras provide sample surface images at approximately 10X and 100X magnification and a chamber image to aid in positioning the samples for measurement. Instrument control and data analysis are performed using ESPRIT software running on a personal computer that is connected to the analyzer.

4 Specimens

Samples as small as 25 μm in diameter can be examined using the instrument. Smaller samples may produce sufficient x-ray emission for measurement if they are positioned within the circle on the video screen aligned with the x-ray optic. If quantitative results are desired, it is necessary to prepare the samples so that they have a flat, smooth surface. The samples must also be sufficiently thick to allow reliable quantitation. In the case of liquid samples, a plastic cup can be used to contain the sample. The flat, upper surface of the liquid will provide the required analysis surface.

5 Equipment/Materials/Reagents

- a. Bruker M4 Tornado X-Ray Fluorescence Spectrometer
- b. Calibration standards:
 - i. Bruker "Nano" standardization block or any commercially pure manganese Certified Reference Material (CRM)
 - ii. FBI-B002 reference block or other zirconium CRM
- c. Mounting materials (optional):
 - i. Graphite planchet
 - ii. Durotak sample mounting adhesive
 - iii. Plastic sample cups (liquid samples)
 - iv. Chemplex X-Ray Mylar (2.5 μm thick) or polypropylene film (6.3 μm thick) or similar
- d. CRMs of alloy similar to the material being analyzed

6 Standards and Controls

Manganese and zirconium standards are used to adjust energy output and to verify adequate performance of the instrument. For quantitation, alloy class comparison, or to establish the absence of an element, CRMs as similar as possible to the material under analysis are used.

7 Sampling

If large numbers of physically indistinguishable samples are received for compositional analysis, a sampling plan may be employed for testing. If the sampling plan will be used to make an inference about the population, then the plan will be based on a statistically valid approach. All of the samples may be tested at the examiner's discretion. Any sampling plan and corresponding procedure used will be recorded in case notes.

8 Procedure

8.1 Basic Operation

The basic operation from a powered-down condition consists of the following steps.

- a. From a cold start, turn on the power to the computer and instrument.
- b. Open the control software ("M4" icon) and follow the on-screen prompts. Several modes that define regions of acquisition are available including Point, Line and Area modes (tabs at top of screen).
- c. If the instrument power has been off longer than 2 weeks, condition each tube to be used at 15 kV, 300 μ A for 5 minutes followed by 25 kV, 300 μ A for 5 minutes before operating at higher power.
- d. Position a specimen using the software drag bars or by entering known position locations. **WARNING:** The stage motion controller adjusts z height first. Assure that specimens will clear the tube guard by moving in x and y directions at low z ($z=50$ mm typical), then adjust the z-height separately. Should the proximity sensor on the tube guard be activated, reset the motion controller by selecting "Reference all" on the "Stage" tab. Sample height must be incorporated in determining stage height to achieve desired working distance.
- e. Verify energy scale linearity:
 - i. Use either tube with no filter, in air or vacuum.
 - ii. In Point mode, acquire signal for 100 s live time on a Zr standard (FBI-002 block or other Zr CRM.)
 - iii. Identify the position of the maximum height of the Zr $K\alpha$ peak. If this energy differs by more than ± 0.05 keV from the expected peak energy of 15.746 keV (the

- weighted average of the Zr $K\alpha_1$ and Zr $K\alpha_2$ emissions), then perform an energy adjustment.
- iv. Energy adjustment: Open the System tab, then Spectrometer tab. Highlight Zr $K\alpha$, select pulse rate of 130,000 cps, and energy ranges of 20 kV and 40 kV. Select Medium (precision), then “START”.
 - v. Verify the position of the Zr $K\alpha$ peak maximum as above. If repeated failure of the energy adjustment routine occurs, the instrument may have to be serviced to correct the problem.
 - vi. Record the verified Zr $K\alpha$ peak position in the instrument log.
- f. Verify energy resolution:
- i. Use either tube at full power with no filter, in air or vacuum.
 - ii. Position a Mn standard (Bruker “Nano” standardization block or other Mn CRM) for measurement.
 - iii. Open the System tab, then Spectrometer tab. Select Mn $K\alpha$, 130,000 cps pulse rate, 40 kV, Medium (precision), then “TEST”.
 - iv. Run long enough to allow the FWHM (full width-half maximum) value to stabilize to one decimal place. If the FWHM value exceeds 148eV, instrument service may be required.
 - v. Record the Mn $K\alpha$ FWHM value in the instrument log.
- g. Verification of the energy linearity and resolution are performed each day prior to the instrument being used for casework. Instrument performance can be re-verified during a long course of testing at the operator’s discretion. Energy adjustment of the instrument will be undertaken whenever the x-ray peak positions differ by more than ± 0.05 keV from their theoretical positions.

8.2 General Analysis

- a. Insert the specimen(s). In Point mode, align the area of interest at the center of the circle displayed on the video image at 10X magnification. Rough surfaces must be placed so that a working distance of ~ 10 mm can be achieved at the region to be analyzed without obstruction from neighboring high points. For a liquid specimen, the surface of the liquid should be within 2 mm of the top of the sample cup.
- b. Select the appropriate measurement atmospheric condition: air or vacuum. Liquids or vacuum sensitive materials must be tested in an air atmosphere. To test in vacuum, select the vacuum icon.

- c. Focus the area to be measured at 100X magnification. An autofocus function is available through an icon adjacent to the video output.
- d. Select the appropriate x-ray tube, tube voltage and current to achieve a dead time of approximately 30% when collecting a spectrum. Acquisition parameters and filters can be adjusted to optimize the analysis conditions. An aluminum alloy, carbon steel and a silver alloy, for example, would all require different operating conditions for optimal results. A set of useful, basic analysis conditions can be found in 9 Instrumental Conditions. It is typical to analyze materials of atomic number 22 (Ti) and below under vacuum atmosphere.
- e. Acquire a spectrum for an appropriate duration to collect sufficient counts for analysis. Acquisition times will depend on the conditions chosen, sample material and the sample area exposed to the incident beam.
- f. Identify the peaks present in the spectrum using the interactive periodic table in the analysis software. Software-generated identifications must be interpreted by an experienced operator to prevent misidentification of energy peaks. The system software automatically filters the escape peaks of predominant elements from the spectral display. Refer to CU Metallurgy SOP *Compositional Analysis by EDXRF* for more details regarding peak labeling.
- g. Print an individual spectrum using the innermost IMPORT-EXPORT menu, print command. This command will generate the filename and acquisition conditions on the printout. Write the resulting percent dead time on this printout. (Although dead time is saved within the raw data file, it will not print automatically.) To print multiple overlaid spectra, highlight and checkmark all of the spectra from the viewing window list before selecting the print command from the innermost IMPORT-EXPORT menu. If not printed on separate, individually printed spectra, record the acquisition conditions for the multiple, overlaid spectra in the case notes.
- h. Ensure the tube power returns to standby (20kv, 50 μ A) after testing is completed. If the instrument will be unused for two or more days, shut off the x-ray tube. Close the software.

8.3 Quantitation of Data

In general, x-ray spectra are not used to generate quantitative data. However, the spectra acquired from a sample can be processed to yield weight concentrations of the elements detected. The ESPRIT analysis software contains several methods for semiquantitative and quantitative

analysis, including standardless fundamental parameters-based and standards-based analysis that can be applied to bulk materials or coating systems. Validation of any of these methods will include analysis of CRMs similar to the material under examination to assess the reliability of the data being generated.

9 Instrumental Conditions

Table 1 contains a set of basic analysis conditions that have been found to be useful for preliminary screening of materials. Other conditions are permissible and will be determined by the operator based on analytical objectives.

Table 1: Basic Operating Parameters for Analysis

<u>Control Tab</u>	<u>Parameter</u>	<u>Value</u>
Spectrometer	Maximum energy	40keV
	Mode	Normal operation
	Cooling	Thermostat
X-ray tube 1 (microfocus tube)	Voltage	40 kV
	Current	250 μ A
	Filter	none
Acquire	Range	40 keV (provides ~10 ev/channel)
	Preset	100 seconds
(Top left icon)	Atmosphere	Vacuum

10 Decision Criteria

10.1 Instrument Performance

Energy adjustment of the instrument will be undertaken whenever the x-ray peak positions differ by more than ± 0.05 keV from their known positions.

10.2 Spectral Analysis

General decision criteria for peak identification, spectral comparison and quantitative EDXRF analysis are described in *Compositional Analysis by EDXRF*. Additional considerations particular to this instrument are:

- a. The Bruker M4 Tornado microfocus x-ray tube with polycapillary lens generates a

Bremsstrahlung excitation spectrum that tails off at the higher end of the spectrum. This inhibits fluorescence of lines with absorption energies greater than 30keV, regardless of any further increase in tube voltage. This can result in significantly higher limits of detection for K line emissions from elements with atomic number of approximately 48 and higher. Conditions may be adjusted to optimize the L and M lines emissions from these elements to aid detection.

- b. Each tube will produce its own characteristic energy peaks, e.g., the rhodium x-ray tube should not be used if Rh is expected to be in the sample and conversely, Rh should not be reported to be present in the sample unless verified. The Mo x-ray tube can be used for verification.
- c. The geometry of the tube-sample-detector arrangement creates diffraction peaks from crystalline materials (including metals). These artifacts in the compositional spectra can usually be readily differentiated from x-ray fluorescence peaks because diffraction peaks appear broader across the energy axis and because their positions often differ from known atomic emissions. When using the microfocus polycapillary tube to analyze steels, the Bruker M4 Tornado often presents a small diffraction peak near 3.5 keV.

11 Calculations

Not applicable.

12 Measurement Uncertainty

Typically, the Bruker M4 Tornado is not used for quantitative analysis. Should it be required, the measurement uncertainty will be estimated in accordance with *Chemistry Unit Procedures for Estimating Measurement Uncertainty* in the CU Quality Assurance and Operations Manual.

13 Limitations

Compositional Analysis by EDXRF contains general limitations of compositional measurement by x-ray fluorescence spectrometry. Additional limitations specific to this instrument are:

- a. Vacuum sensitive samples, like liquids, that are suspected of containing elements with atomic number $Z < 22$ (Ti) cannot be measured in the Bruker M4 Tornado. These can be measured in a system offering a helium overpressure atmosphere.

- b. Spectral artifacts, including diffraction peaks, must be considered during analysis. (See 10.2 Spectral Analysis).

14 Safety

- a. The Bruker M4 Tornado produces x-rays. Wear an x-ray film badge or dosimeter when operating this instrument. The instrument has a protective enclosure with internal safety interlocks to prevent inadvertent x-ray radiation exposure. Never bypass or disable the safety interlocks on this instrument.
- b. The detector and tube windows are comprised of beryllium and are extremely delicate. In the event of damage to a window, the beryllium dust created could pose an acute health hazard. If this occurs, seal the chamber and seek assistance from the Laboratory Health and Safety Group.

15 References

Jenkins, R., *X-ray Fluorescence Spectroscopy*, Wiley Interscience, New York 1988

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Margui, E. and Van Grieken, R., *X-Ray Fluorescence Spectrometry and Related Techniques*, Momentum Press LLC, New York 2013

Chemistry Unit Quality Assurance and Operations Manual, Federal Bureau of Investigation, Laboratory Division, latest revision

Compositional Analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF), CU Metallurgy SOP Manual, latest revision

FBI Laboratory Quality Assurance Manual, Federal Bureau of Investigation, Laboratory Division, latest revision

FBI Laboratory Operations Manual, Federal Bureau of Investigation, Laboratory Division, latest revision

Rev. #	Issue Date	History
1	03/15/2016	Added references to a second x-ray tube option (Sections 1, 3 8.2d-e, 9-Table 1, 10.2b and 14b). Clarified spectrometer verification routine (Section 8.1c-g). Corrected terminology (Section 8.2h).
2	03/02/2018	Renumbered Metallurgy SOP Manual documents. This document was formerly Metal 27 and is now designated Metal 502. Added personnel to section 2. Clarified application of instrumental conditions, Section 9. Made minor editorial corrections throughout document. Added requirement for sampling plan retention in section 7. Revised sections 8.1.e and 8.1.f to clarify instrument verification procedure. Added instrument shut-down directions in section 8.2.h. Added section 10.2.b to clarify x-ray tube influence. Updated safety requirements in section 14. Added additional references to section 15.

Approval

Redacted - Signatures on File

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