

REX Evaluation Guide



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I. INTRODUCTION

REX™ (RReal-time Elemental X-ray Fluorescence System) is the only instrument capable of unattended real-time elemental analysis of dissolved metallic contents in fluids using X-ray fluorescence with low parts-per-billion (ppb) sensitivity. Important applications exist for the following industries, among others:

- Municipal drinking water supply
- Chemical processing industry
- Mining and petroleum
- Pharmaceuticals and food processing
- Ultra-pure cooling and wash water intake monitoring
- Waste water recovery monitoring
- Environmental regulatory monitoring

The system is highly compact and fully automated. Once installed into a flow stream, it can be set to automatically provide regular readings of concentration levels of metallic elements of interest in the flow stream to be monitored. It can also be programmed to set an alert when preset levels were exceeded for immediate processing attention. This capability offers significant advantages over present state-of-the-art for elemental analysis that requires samples to be taken to be analyzed in a laboratory by trained technicians with long turn-around time, lacking in ability for continuous monitoring and timely alert, and costly in per-sample analysis costs for personnel time and consumables. In contrast, REX requires no consumables, fully automatic and can be highly cost competitive, amortized over time.

In this REX Evaluation Guide, a description of the instrument and its operating principles is described in Section II. Operation of the instrument, data processing for automated operation, and data output are described in Section III. Useful links for additional information are provided in Section IV. An example of raw data collected by the instrument is included in the Appendix.

II. DESCRIPTION OF REX

The sensitivity of standard X-ray fluorescence instruments for detection of elements is generally limited to high parts-per-million (ppm) level. REX is able to achieve low ppb level sensitivity by a patented design using a proprietary system based on two well established scientific principles: capacitive deionization and X-ray fluorescence (See Section IV).

Figure 1a shows the frontal view of the instrument. The unit is fully enclosed in a radiation-safe shielded enclosure that measures 42 cm wide by 47 cm deep and a maximum height of 43 cm. The weight of the unit is 18 kg. All connectors are located in the rear of the unit as shown in Figure 1b. Starting from the right, the two white knobs are the connectors for in and out flow of the fluid stream to be analyzed. Typically a 40 mL/min stream is diverted from the flow stream to be monitored; this rate can be

manually adjusted using a needle valve. A manifold with a replaceable 5 micron filter is provided as an accessory for installation before the inflow connector. To the left of the two flow connectors is the connector for any process controller unit(s) (four AC/DC 7 amp relay contact sets), followed by a USB connector and two Ethernet connectors for external communication, and a power cord followed by two indicator lights, one for power on indication and the other for fault conditions (e.g. opened interlock switch). The enclosure is fully secured for radiation and high voltage electrical safety. Any service is to be performed only at the factory through an express shipping/direct exchange program, or by an AMDS technical support specialist via remote network connection.



The element of the REX instrument which enables it to detect and quantify concentrations to low ppb level using standard X-ray fluorescence methods is the patented concentration cell, utilizing a proprietary nanocellular porous material to reversibly concentrate dissolved metals via the capacitive deionization process. The nanocellular material is engineered to have an extremely large amount of surface area per unit volume, typically on the order of 400 square meters per gram. The large surface area allows the ions to be captured on the surface of the material, and ion concentration increases predictably as a function of the concentration time. The concentration cell is a relatively simple device with a flow channel into a cell containing the nanocellular material in the form of an electrical capacitor to which a voltage can be applied. The basic arrangement is shown schematically in Fig. 2, with an X-ray source directed onto the nanocellular cell and an energy dispersive detector to collect and count photons.

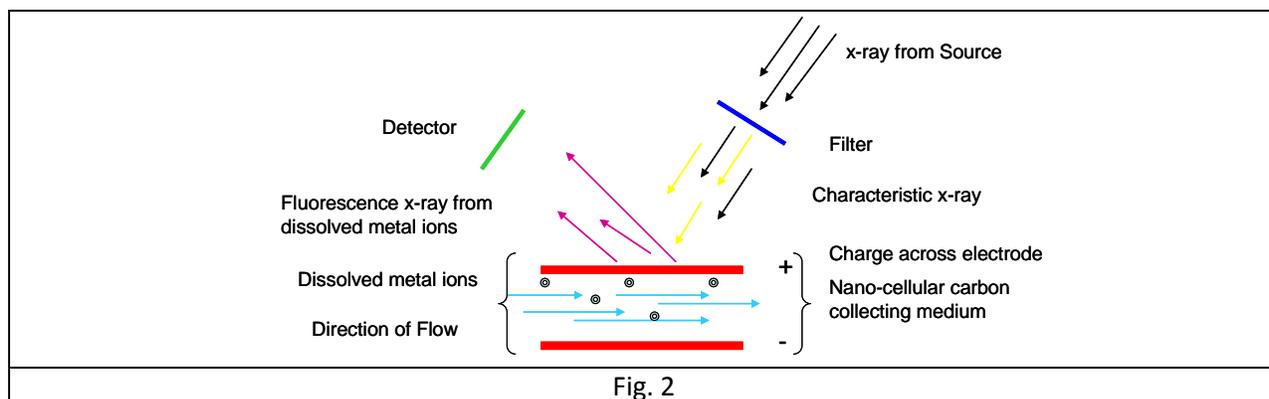


Fig. 2

In operation, with a voltage applied to the capacitor and the fluid flowing through the concentration cell, the dissolved metal ions are collected on the surfaces of the nanocellular capacitor. For a flow stream with very low concentration of dissolved metal that would normally be undetectable by X-ray fluorescence, the concentration step would bring the concentration of the analyte of interest up to detectable levels. The concentration can then be quantified by scaling the measured signal using a database of known signal characteristics of each element of interest.

The concentration cell will concentrate all dissolved metals present in the flow stream. A typical X-ray fluorescence spectrum, including background, is as shown in Figure 3, with signature wavelength (photon energy) of some of the elements present shown to allow for identification.

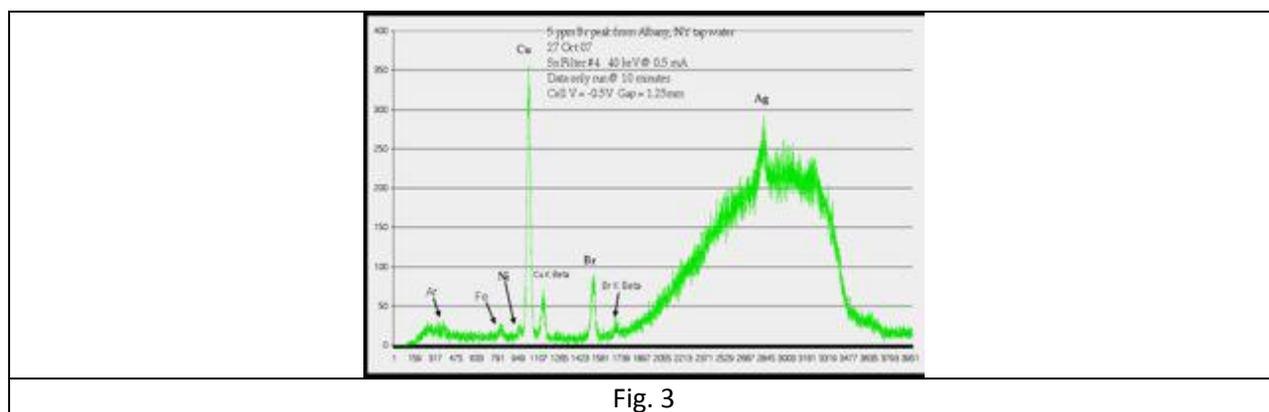


Fig. 3

The rate of concentration of each element is dependent on the applied voltage, the flow rate, and the respective electrochemistry of each element. To quantitatively determine the concentration of each element of interest, a custom database is compiled for each instrument to determine the concentration for each element as a function of signal, flow rate, and applied voltage. This database is used as an integral part of the processing algorithm.

After completion of data collection, the system can be automatically cycled through a self-cleaning process to remove the collected ions from the cell. This enables the system to be ready for repeated

monitoring of the concentrations in the flow stream. Details of the data collection process are further described in the next section.

III. DESCRIPTION OF DATA COLLECTION PROCEDURES

The data collection process generally consists of several fully automated steps and is described in the following subsections. Upon powering up the REX, the system automatically cycles through these steps based on preset or user specified protocols.

A. Background Survey

Prior to each measurement cycle, a background spectrum is taken to establish the background signal intensity. The primary source of background signal is scattering of the X-ray from the source. The background is taken with the X-ray source turned on and with the same fluid flowing through the concentration cell but without the applied voltage that would collect any dissolved metal ions in the flow stream. The background signal is read for a specified period of time, stored for subsequent data processing, and then archived at the end of the analysis cycle.

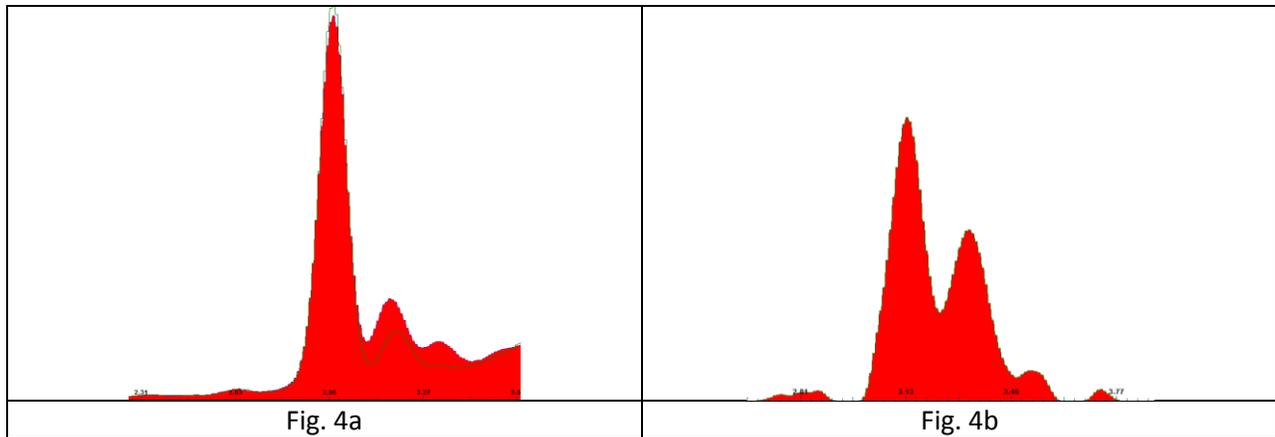
B. Data Collection

After completion of the background survey, the system is then switched to the analytical data collection cycle with the X-ray off to allow the concentration of the dissolved ions to build up with the applied voltage turned on. Based on the anticipated concentration in the flow stream, the concentration time is preset. If the anticipated concentration is unknown, the system can be set to sample the concentration by intermittently turning on the X-ray to determine if the concentration has reached a detectable level, or alternatively by monitoring the electrical conductivity of the concentration cell which provides information regarding the total concentration of collected ions. The limits of detection (LOD) for different elements of interest for the instrument are dependent upon the relative concentration rate for the different elements, and total concentration time.

Following the concentration step, the X-ray source is turned on to collect spectrum data. Collected photons are sorted by energy and cumulatively counted over the same period of time as for background data. The result is a set of raw data, ready for processing.

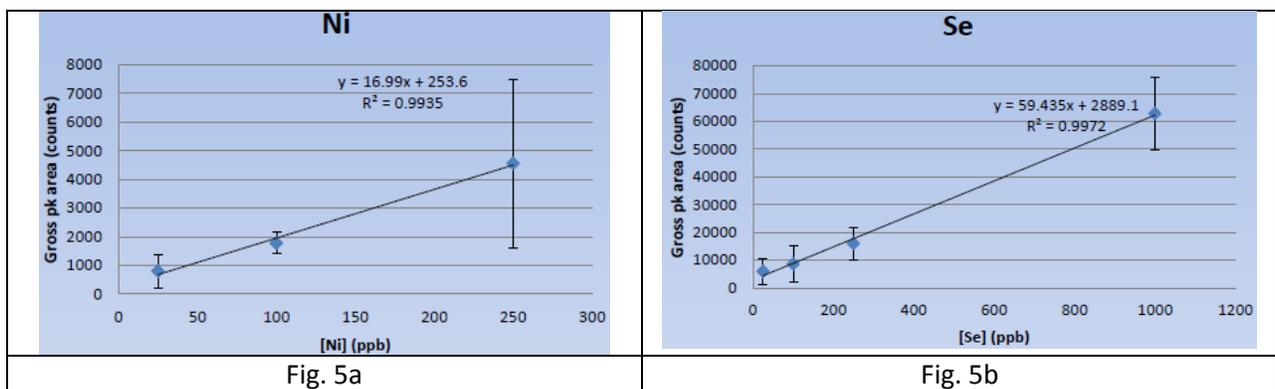
C. Data Reduction

The collected data include both background noise and signal from the X-ray fluorescence of the element present. An example of the portion of the spectrum for Cd including background and with background-subtracted signal is shown in Figs. 4a and 4b respectively. This example is chosen to illustrate the very high peak attributed to Ar in the air in close proximity of the Cd signal of interest, and the relatively small difference between the Cd signal and the background.



The first step in data extraction is to subtract the background spectrum from the analytical spectrum. The data are reported to 3-sigma level such that 99.7% of the measurements are within the stated error. This 3-sigma uncertainty is determined based upon statistical uncertainty in the spectrum data established during instrument calibration along with observed variation within the background spectra from run to run.

The next step is to quantify the concentration based on the amplitude of the background-subtracted signal from each element. Built into the processing software is a database of calibration curves for each element of interest. Two examples of the calibration data for Se and Ni used in generating quantitative measurements of the concentration in the flow stream are shown in Figs. 5a and 5b, respectively. They show the photon counts accumulated over a specific period of time plotted as a function of known concentration of the specific element. From the data, the LOD for the element is calculated based upon magnitude of analytical signal relative to the noise measured during replicate runs with zero analyte present.



In Figs. 5a and 5b, each data point represents data collected using a sample of known concentration. The error bar is the calculated 3-sigma uncertainty yielding a 99.7% confidence interval for the data variability. The trend curve is derived from the data yielding the trend line formula for 'y' as shown, and the correlation coefficient (R^2) illustrates the goodness of fit, with $R^2=1$ corresponding to perfect fit. As has been noted, because the nanocellular capacitor has a very large surface area for collection of the

ions, the counts over a period of time is a linear function of the concentration for samples of low concentration below the parts-per-million (ppm) level, which allows for simple scaling of the data to determine analyte concentration in the parts-per-billion ranges.

Using the database built into the processing algorithm, quantitative determination of the concentration in the unknown sample is readily determined from the number of photon counts associated with the element over the concentration time by scaling the signal based upon the counting time and collection voltage used for ion collection.

D. Data Output

The output of the instrument is a report on the concentration of each metal present in the flow stream reported to 3-sigma. Output options include:

- Text file
- Wireless alerts to phones or computers
- Satellite uplink from installations at remote locations

A sample output report is shown in Fig. 6 with concentration exceeding threshold values highlighted. The frequency of analysis and elements to be measured can be user selected.

Date:	June 2, 2008	
Time:	2:15 PM	
Location:	Process Water	
	EPA	
Metal	Limit, ppb	Analysis, ppb
Antimony	6	ND
Arsenic	10	3
Barium	2,000	120
Vanadium	15	40
Cadmium	5	ND
Chromium	100	5
Lead	15	30
Mercury	2	ND
Selenium	50	ND
Thallium	2	ND

Fig. 6

E. Self-Cleaning

In order to provide a fully automated system for continuous real-time measurement of dissolved metals, the processing cycle includes a self-cleaning step. The purpose of the self-cleaning step is to remove the ions that have been deposited on the surface of the nanocellular capacitor during the previous analysis cycle. In this step, the instrument simply shorts out the capacitor while allowing the flow stream to continue. Without the applied voltage, the collected ions are released from the surfaces and washed out by the flow stream.

Typically, the cleaning step is run for the same duration as for the concentration step. Upon completion of the cleaning step, the system is ready for next measurement, either immediately for continuous monitoring, or at a later point if less frequent analyses are desired. For each analysis, the process starts with a background survey such that any residue from the previous measurement will be part of the background and subtracted out to ensure accuracy of the data.

IV. USEFUL LINKS

A companion video that explains the operation of the REX system can be found at:

https://s3.amazonaws.com/AMDS/AMDS_demo-fullsize.m4v

A PowerPoint presentation describing American Micro Detection Systems, Inc. and the REX product can be found at:

<https://s3.amazonaws.com/AMDS/February-mkting-slides.pdf>

A tutorial on X-ray fluorescence for elemental analysis, including signature photon energies of elements for XRF detection can be found on Wikipedia at:

http://en.wikipedia.org/wiki/X-ray_fluorescence

A brief tutorial on membrane-based capacitive deionization can be found at:

http://en.wikipedia.org/wiki/Capacitive_deionization

APPENDIX

SAMPLE DATA FOR 250 ppb Ni

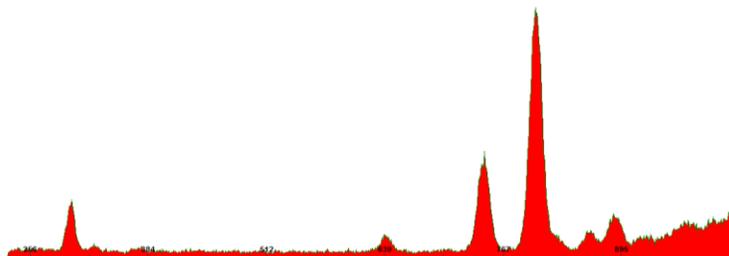


Figure 1A: Blank (or Background) spectrum of solution with 250 ppb Ni. Note the presence of multiple peaks within the sample, attributed to Ar in the air and Fe, Ni, and Cu in the instrument's optics.

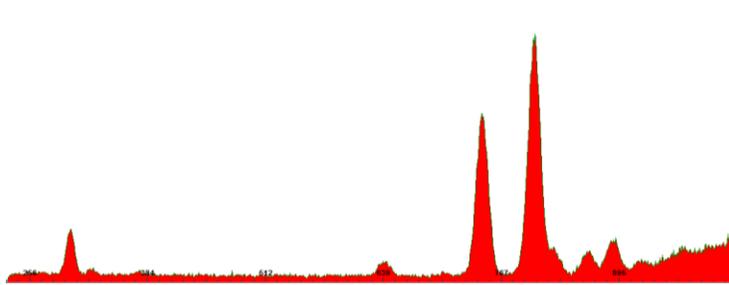


Figure 1B: Analytical spectrum of solution with 250 ppb Ni. Note the relative increase in signal for one of the main peaks, at an energy level corresponding to the K_{α} line for Ni (7.478 keV).



Figure 1C: Blank-subtracted analytical spectrum of solution with 250 ppb Ni. The Ni signal is clearly evident after subtracting the blank signal, with K_{α} and K_{β} peaks visible at energies of 7.478 and 8.265 keV respectively.