

### Ultra-trace X-ray Analysis of Martian Rocks and Soils using Low-cost Commodity Hardware

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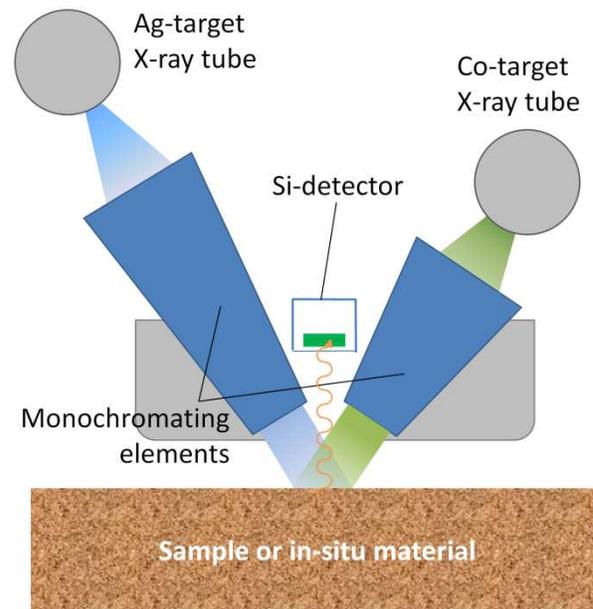
**Summary:** We describe an X-ray fluorescence (XRF) system capable of measuring all elements heavier than sodium, with detection limits below one part-per-million (1 ppm) for a wide range of elements and as low as 0.04 ppm in ideal cases. By analyzing the energy profile of inelastically scattered X-rays, it is also possible to simultaneously determine the total light element (H-C-N-O) content of the material being measured. The system could be straightforwardly extended to carry out energy-dispersive X-ray diffraction analysis to determine the major mineralogical constituents of the samples being measured. The entire system would be constructed from low-cost, light-weight, commercially available components.

**Our research group:** CSIRO is the Australian Government's national research agency. For more than three decades, our group has focussed on developing novel instruments to solve challenging measurement and imaging problems for the minerals and security industries. We develop new systems from initial concept through to commercial application. Most recently, we have developed and successfully operated a robust XRF system for on-stream analysis of sub-ppm levels of high-value platinum-group elements in a minerals-processing plant.

**Background:** Recent Mars missions have included an alpha-particle X-ray spectrometer (APXS) for sample composition analysis [1,2]. The APXS uses sealed  $^{244}\text{Cm}$  radioisotope sources and silicon detectors to register fluorescent X-rays, scattered alpha particles and induced protons. The spectrum for light elements is complex, due to overlaps of closely spaced lines. Detection limits for heavy elements are reported [2] to be 100 ppm for Ni and 20 ppm for Br with a 3-hour measurement time.

**Proposed instrument design:** Our proposed design is shown in figure 1. A combination of low-power X-ray tubes with monochromating X-ray optical elements provide a high flux of quasi-monoenergetic X-rays on the sample. One tube would have a cobalt-target and be operated to produce a photon flux at 6.9 keV, providing optimal excitation of light elements. The second tube would use a silver target and be operated to produce a photon flux at 22 keV, providing strong excitation of a wide range of elements from iron to uranium. A single high-resolution X-ray detector with optional Peltier cooling would measure the fluorescent X-ray spectrum from either source. Miniature X-ray sources with a total system mass of

360 g and power consumption below 5W at 2W beam power are available commercially. Similarly, we propose using a commercial Si-detector/digital spectrometer (mass 180 g, 2.5 W power consumption) similar to those that have been successfully used on previous Mars missions.

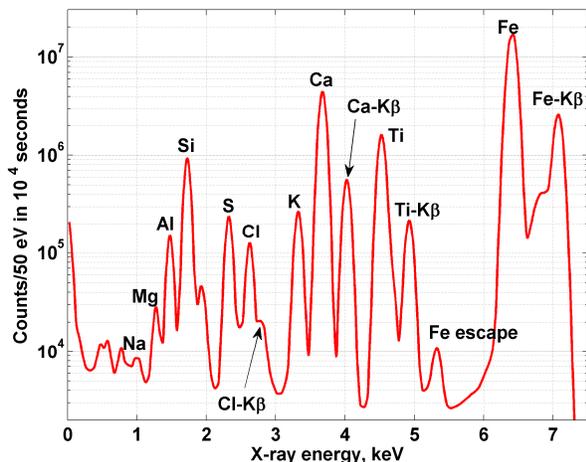


**Figure 1. Sketch of proposed XRF instrument design.**

**System modeling:** We have conducted detailed computed modeling of the proposed design, using a version of the EGSnrc [3] code, modified to improve the accuracy of X-ray fluorescence physics [4]. The model includes a detailed description of the X-ray source, optical elements, sample material and detector and includes resolution and incomplete charge collection effects. Our modeling code has been extensively benchmarked against experimental measurements of similar systems.

**Major element detection:** Figure 2 plots a simulated X-ray spectrum using the Co target X-ray tube. The primary excitation energy is 6.9 keV, although a smaller flux of X-rays at 13.8 keV is also present. The primary energy is chosen to lie below the iron K-edge, reducing the otherwise overwhelming intensity of the iron fluorescence lines. A detector resolution of 130 eV at 5.9 keV is assumed. Figure 1 plots the simulated X-ray spectrum for a Martian rock of typical composition [5]. Peaks for all simulated elements are visible and well resolved.

Statistical errors on peak intensities for a 5-minute integration time are below 1% for elements in the range Mg-Fe; for Na, the error is approximately 10%. A few minutes would therefore suffice for a measurement of major elements.



**Figure 2.** Simulated X-ray fluorescence spectrum for rock of composition 1.3% NaO, 7.3% MgO, 8.4% Al<sub>2</sub>O<sub>3</sub>, 52.3% SiO<sub>2</sub>, 5.2% SO<sub>3</sub>, 0.6% Cl, 0.5% K<sub>2</sub>O, 6.0% CaO, 1.3% TiO<sub>2</sub> and 17.1% Fe<sub>2</sub>O<sub>3</sub>.

**Trace element detection:** To explore the trace-element detection limits of our proposed instrument, we simulated the addition of 20 elements from Cu ( $Z=29$ ) to U ( $Z=92$ ) to our basic Martian rock composition. Lowest detection limits are generally obtained for elements having X-ray fluorescence lines above the bright iron lines at 6-7 keV. The silver-target secondary X-ray source is used to excite elements with K-series or L-series lines in the range 7-19 keV. For these elements, covering Cu-Mo via their K-series X-rays and Dy-U via their L-series lines, 3-sigma detection limits for a 10,000 second (approximately 3-hour) measurement time are significantly below 1 ppm. Elements in the range Ru-Gd can only be measured via their L-series fluorescence lines which lie in the energy range 2.5-6.5 keV. These lines overlap with the strong lines from major elements in the sample, leading to higher detection limits in the range of 1-25 ppm. Table 1 summarises these estimated detection limits.

**Light element detection:** We have previously demonstrated [6] that analysis of the shape of the energy spectrum of inelastically scattered X-rays can provide accurate information on the proportion of very light elements (H-C-N-O) in a sample. Together with information obtained from Rayleigh/Compton scatter ratios and the proportions of elements heavier than Na obtained via XRF, we anticipate that approximate information about levels of water of hydration, carbonates or nitrates could be inferred.

**Table 1.** Estimated  $3\sigma$  detection limits for trace elements; a 10,000 second measurement time is assumed.

| Element | Z  | DL (ppm) | Element | Z  | DL (ppm) |
|---------|----|----------|---------|----|----------|
| Cu      | 29 | 0.28     | La      | 57 | 22       |
| Ge      | 32 | 0.064    | Nd      | 60 | 8.1      |
| Br      | 35 | 0.047    | Gd      | 64 | 10.7     |
| Sr      | 38 | 0.039    | Tm      | 69 | 0.65     |
| Mo      | 42 | 0.068    | W       | 74 | 0.27     |
| Pd      | 46 | 1.3      | Au      | 79 | 0.10     |
| Sn      | 50 | 1.5      | Pb      | 82 | 0.083    |
| I       | 53 | 19       | U       | 92 | 0.044    |

**Mineralogical analysis:** We have previously demonstrated [7] that a compact, energy-dispersive X-ray diffraction spectrometer can be constructed using a low-power X-ray tube and small, high-resolution detector. The miniature X-ray tubes proposed for use in the XRF spectrometer emit X-rays over a wide cone-angle, which would allow the silver-target tube to be simultaneously used for XRF and XRD analysis of separate samples. A second Si-detector would be used to measure the energy spectrum of X-rays diffracted through a small, fixed-angle, allowing a diffraction spectrum with a d-spacing resolution of a few percent to be obtained. We anticipate a performance similar to that reported for the CheMin instrument on the current MSL mission.

**Summary:** The trace-element X-ray fluorescence technology developed over the past decade by CSIRO could be used to obtain in-situ analysis of Martian rock and soil samples with more than 100 times the sensitivity of instruments used on previous missions. Such an instrument would allow a wide range of geologically significant elements to be measured that to date have only been observable in recovered Martian meteorites. The instrument could be constructed from low-cost, light-weight and low-power, commercially available components. The elemental analyser could be augmented with an additional detector to provide mineralogical information via energy-dispersive X-ray diffraction.

**References:** [1] R. Gellert *et al* (2006) *J. Geophys. Res.* 2006, 111, E02S05. [2] APXS science report, <http://msl-scicorner.jpl.nasa.gov/Instruments/APXS> [3] I. Kawrakov *et al* (2011) *NRCC report PIRS-701* [4] G. Roach, J. Tickner and Y. Van Haarlem (2012, in press), *X-ray spectrometry*. [5] R. Rieder *et al* (1997), *Science*, 278 no 5344, 1771-1774. [6] J. Tickner and G. Roach (2004) *Nucl. Instr. Meth. B*, 213, 507-510. [7] J. O'Dwyer and J. Tickner (2008) *Appl. Rad. Iso.* 66(10), 1359-1362.