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Nuclear Instruments and Methods in Physics Research A 559 (2006) 776–778
NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A
www.elsevier.com/locate/nima

A 36-pixel superconducting tunnel junction soft X-ray detector for environmental science applications

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Available online 6 January 2006

Abstract

We are operating a superconducting tunnel junction detector for high-resolution soft X-ray spectroscopy at the Advanced Biological and Environmental X-ray Facility at the Advanced Light Source synchrotron. We have recently upgraded the instrument from 9 to 36 pixels for increased sensitivity. We have also acquired a new digital signal readout to increase the total count rate capabilities to $\sim 10^6$ counts/s while maintaining a high peak-to-background ratio. We report on the performance of the spectrometer, and discuss speciation measurements of chromium in welding aerosols as a typical application of the instrument in environmental science.

PACS: 07.85.Nc; 85.30.M

Keywords: Superconducting tunnel junctions; Soft X-ray absorption spectroscopy; Digital signal processors; Chromium speciation

1. Introduction

The oxidation state of metals in environmental contaminations determines their solubility and thus their bioavailability and toxicity. Synchrotron-based X-ray absorption spectroscopy (XAS) is widely used to measure oxidation states by scanning a monochromatic X-ray beam through an absorption edge of the element of interest. No chemical sample processing is required for XAS analysis, thereby eliminating possible oxidation state modifications during sample preparation that affect other techniques such as wet-chemical separation. For dilute samples, the XAS sensitivity is highest if the subsequent fluorescence is recorded as a measure of absorption, provided an X-ray detector is used that can separate the weak emission line from the background fluorescence.

We are developing high-resolution high-speed superconducting tunnel junction (STJ) X-ray detectors for the soft XAS band below ~1 keV [1]. Soft X-ray L-edge spectroscopy provides higher sensitivity for oxidation state measurements than the more commonly used metal K-edges in the hard X-ray band, because natural line widths are narrower at low energies and chemical shifts per change in oxidation state are larger [2,3]. Here we discuss recent upgrades of our STJ spectrometer to increase its sensitivity, and illustrate its potential for environmental science applications with measurements of the chromium oxidation state in welding aerosols.

2. Spectrometer performance

We operate our STJ soft X-ray spectrometer for fluorescence-detected XAS at beam line 4.0.2 at the Advanced Light Source synchrotron [4]. The sensor consists of four 3×3 arrays of $200 \times 200\,\mu m^2$ Nb-Al-AlOx-Al-Nb STJs. The arrays are held at a temperature below 0.4 K at the end of a cold finger of a two-stage adiabatic demagnetization refrigerator, and subtend a solid angle $\Omega/4\pi \approx 5 \times 10^{-4}$ [1].

X-ray absorption spectra are acquired by stepping the energy of the monochromatic synchrotron beam over an

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0168-9002/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.nima.2005.12.135

electron binding energy of the element of interest and recording the subsequent fluorescence signal, i.e. by counting the number of events in an energy window around the emission line for each excitation energy over the 10 s acquisition time. The sensitivity of the measurement is determined by the number of signal and background counts in this energy window. Since the STJ efficiently removes background counts caused by line overlap, the sensitivity in our measurements is set by the maximum acquisition rate and the white spectral background [5]. At high count rates, this spectral background is often determined by pile-up and thus by the performance of the pile-up rejection used (Fig. 1).

We are, therefore, collaborating with X-ray Instrumentation Associates [6] on the development of digital signal processors (DSPs) for STJ readout. These DSPs continuously sample the STJ pre-amp output with a 100 MHz 14-bit A/D converter and calculate three moving averages, one before, one during, and one after the signal rise. The first and third average extend over a user-selectable peaking time τ_{peak}, and the middle one over a gap time τ_{gap}. These three averages are converted by a fast field programmable gate array to a pulse height signal, given by the difference between the averages before and after the pulse rise, with corrections due to the finite pulse rise and decay times. If both rise time and decay time of the signal pulse are known and follow a simple exponential form, the pulse height can be extracted with at least the same precision as with commercial analog shaping amplifiers.

This pulse height algorithm does not require the waveforms to decay to zero as long as the peaking time τ_{peak} is shorter than the pulse decay time, and allows operating the STJ spectrometer at rates up to 30,000 counts/s per pixel (Fig. 1). In addition, the pile-up inspection routines are significantly more efficient than those of our earlier analog shaping amplifier, and can reduce the white background in our spectra by an order of magnitude. This increases the sensitivity of our STJ spectrometer accordingly, and extends the range of L-edge XAS to samples with metal concentrations well below 100 ppm.

3. Chromium speciation in welding aerosols

As an example for measuring metal speciation by XAS with our STJ detector we consider chromium in aerosols generated by welding operations. Under environmental conditions, Cr is stable in two oxidation states, as insoluble and benign Cr(III) and as soluble and carcinogenic Cr(VI). Public concern about Cr(VI) toxicity is pushing towards a reduction in Cr use and release, and towards a better characterization of remaining emissions. One particular concern is the release of Cr in welding aerosols, since inhaled Cr enters the bloodstream directly through the lungs without being reduced in the stomach.

We have characterized aerosol particles produced by gas metal arc welding (GMAW) by XAS on the Cr L-edges [7]. Samples were collected on carbon filters in the exhaust of an enclosed GMAW setup, a widely used technique operated in a controlled environment under standard conditions. A welding dust reference sample from the European Union with known and intentionally high amounts of Cr(III) and Cr(VI) was analyzed for comparison. Fig. 2 shows the absorption spectra of the two

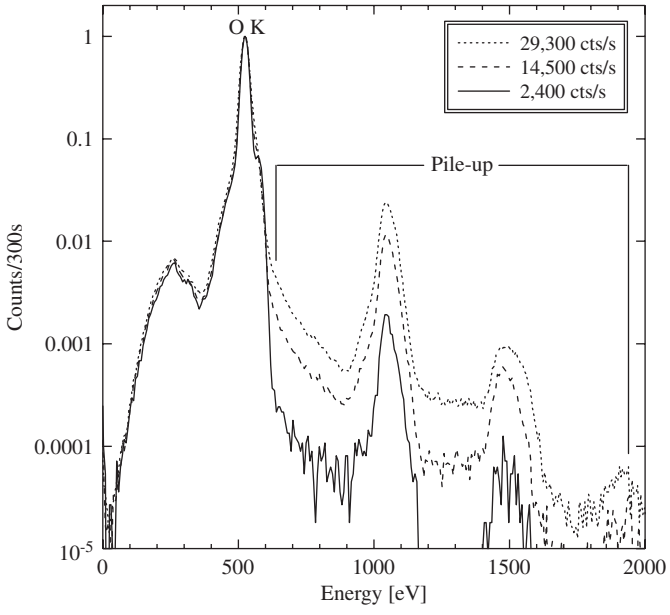

Fig. 1. Fluorescence spectra of an Al_2O_3 sample excited at $E = 700$ eV with different intensity synchrotron beams and acquired with DSP readout. Only oxygen fluorescence is generated, so that the counts above ~600 eV are completely dominated by pile-up.

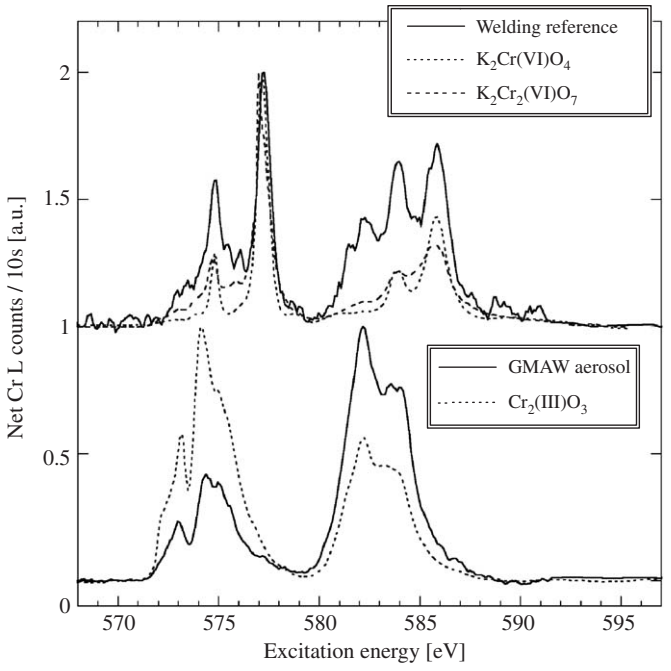

Fig. 2. Fluorescence-detected X-ray absorption spectra of welding aerosols at the Cr L-edges, compared to spectra of environmentally common Cr(III) (bottom) and Cr(VI) (top) model compounds.

aerosols, normalized by the intensity of the incident beam with the background subtracted, and of typical Cr(III) and Cr(VI) model compounds. As expected, the European reference sample contains significant amounts of Cr(VI) as demonstrated by the sharp characteristic peaks at 577 and 586 eV. In contrast, the lack of any absorption features at those energies in the GMAW aerosol indicates a Cr(VI) fraction of less than ~2%. This significantly reduces the concern about the toxicity of Cr generated by gas metal arc welding.

4. Summary

We have built a 36-pixel STJ soft X-ray spectrometer for synchrotron-based high-resolution XAS. It has an energy resolution of ~10–20 eV FWHM below ~1 keV, covers a solid angle $\Omega/4\pi \approx 5 \times 10^{-4}$, and a novel DSP readout allows operation at total rates up to $\sim 10^6$ counts/s with high peak-to-background ratio. We are using the spectrometer for speciation measurements on, for example, heavy metal contaminations to better understand their toxicity and environmental impact.

Acknowledgments

We thank William Heoung and Daniel P. Y. Chang for providing the aerosol samples. We gratefully acknowledge support from the University of California CLE Program, the National Science Foundation under grant DMR0114216, and the DOE Office of Biological and Environmental Science. Part of this work has been performed under the auspices of the US Department of Energy by University of California Lawrence Livermore National Laboratory under Contract no. W-7405-Eng-48.

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