Available online at www.sciencedirect.com
ScienceDirect
Micron 39 (2008) 88–94
micron
www.elsevier.com/locate/micron

Review

WDS versus silicon drift detector EDS: A case report for the comparison of quantitative chemical analyses of natural silicate minerals

H. Evren Çubukçu, Orkun Ersoy, Erkan Aydar *, Uner Çakir

Hacettepe University, Department of Geological Engineering, 06800 Beytepe, Ankara, Turkey

Received 7 September 2006; received in revised form 31 October 2006; accepted 7 November 2006

Abstract

Electron probe microanalysis (EPMA) is an essential analytical approach to determine elemental concentrations of various solid specimens quantitatively in mineralogical, petrological and materials research. Either wavelength dispersive X-ray (WDS) or energy dispersive X-ray (EDS) spectrometric techniques can collect the characteristic X-rays generated from each element in the specimen by an incident electron beam in order to define chemical constituents. Although WDS has been the preferred technique because of its higher spectral resolution and ability to detect trace elements, new generation EDS systems with silicon drift detectors (SDD), equipped with thin windows and integrated digital processing electronics, are claimed to approach the WDS throughput. In this study, we compared the analytical capability of a SDD EDS system with respect to WDS equipped systems on natural silicate minerals. For this purpose, natural rock samples, in which the silicate minerals present had already been analysed by various WDS systems, were chosen to compare these results with the ones acquired with a SDD EDS system. SDD EDS yielded satisfactory results for major elements (Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe) compared with the results of the same minerals obtained by various WDS systems.

Keywords: WDS; EDS; Mineral analyses; Chemistry

Contents

1. Introduction

The chemical compositions of rock-forming minerals maintain crucial information on the temperature, pressure and chemical conditions as well as their temporal variation during crystallization. Therefore, it is vital to determine elemental distribution within minerals in order to understand and interpret the rock-forming processes. Once the chemical data have been acquired from the minerals, a broad range of applications can be realized.

Electron probe microanalysis (EPMA) has become the primary choice of researchers of various fields for its high sensitivity in micrometer scale while permitting to investigate the specimen without being destructed. This technique is based on the electron excited X-ray spectrometry. The characteristic X-rays of each element in the specimen generated by an incident electron beam can be analysed by various detection systems. Dominantly, wavelength dispersive spectrometer (WDS) and energy dispersive spectrometer (EDS) are used in EPMA technique. WDS equipped systems use diffracting

* Corresponding author. Tel.: +90 312 297 77 00.
E-mail address: eaydar@hacettepe.edu.tr (E. Aydar).

0968-4328/$ – see front matter
doi:10.1016/j.micron.2006.11.004

crystals for X-ray discrimination and have X-ray resolutions approximately 10 eV, therefore, chemical detection limits are 100 ppm or better. Whereas EDS systems excel at qualitative analysis since they can acquire spectra covering large energy ranges all at once, but their inferior X-ray energy resolution (approximately 130 eV) limits their use for most applications to analyze concentrations above 0.1% (Scott, 2003). As a consequence of increasing interest in elementary particle detection and semiconductor technology, new silicon detectors have been developed. In 1983, Gatti and Rehak proposed silicon drift detectors (SDDs) as high-resolution position-sensitive detectors for fast ionizing particles and for spectroscopy of X-rays (Gatti and Rehak, 2005). High efficiency, large detection area, position-sensitivity and good energy resolution (125–129 eV, full peak width at half the maximum peak intensity FWHM at Mn Kα: 5 890 eV; Newbury, 2002) make this detector suitable for many applications (Allier et al., 1998). Furthermore, the ability of these detectors to operate at room temperatures, being cooled down with vibrationless peltier technology rather than liquid nitrogen would be an appealing advantage.

It was demonstrated by Reed and Ware (1973) and by later works (i.e. Dunham and Wilkinson, 1978) that quantitative analysis of silicate minerals for elements with atomic number 11 and above could be achieved by EDS with limit of detection around 0.001 mass fraction and with an accuracy equivalent to WDS (Statham, 2002). However, so far as we are aware, no mineralogical study on silicate minerals comparing SDD EDS versus WDS including the treatment of data in a mineralogical practise has yet published. For this purpose, natural rock samples, in which the silicate minerals present had already been analyzed by various WDS systems, were chosen to compare these results with the ones acquired with a standardless SDD EDS system.

2. Analytical conditions and material

WDS analyses have been carried out on various equipments in two laboratories. Cameca Camebax and Cameca SX-100 equipped with 2 and 4 WDS, respectively, are installed in Blaise Pascal University, Laboratoire Magmas et Volcans (LMV), Clermont-Ferrand, France. Cameca SU-30 equipped with 1 WDS and Zeiss EVO-50 with Bruker-Axs XFlash 3001 SDD EDS are installed in Hacettepe University, Department of Geological Engineering, Ankara, Turkiye.

All WDS systems were calibrated with the standards depicted in Table 1. Since XFlash 3001 SDD EDS has an automatic ‘‘strobed’’ zero energy measurement which effectively provides a reference peak corresponding to zero energy, its calibration was achieved using a spectrum with just a single Cu Kα peak (Statham, 2002) with approximately 200,000 counts.

XFlash 3001 SDD EDS was operated in standardless analysis mode. However, with the increased application of standardless analysis, ‘‘out-of-the-box’’ with no customised installation, results are vulnerable to error, particularly when microanalysis is used outside the well-investigated territory of 1–10 keV energy and 15–25 kV accelerating voltage (Statham, 2002). In this study the equipment used was installed regarding the actual physical parameters. Besides, the elements of interest (Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe) are within the 1–10 keV limits.

Analytical conditions during analyses are set as follows: 15 kV accelerating voltage, 10–12 nA beam current with 5 μm beam diameter for Cameca Camebax, 15 kV accelerating voltage, 15 nA beam current with 5 μm beam diameter for Cameca SX-100, 15 kV accelerating voltage, 18 nA beam current with 3 μm beam diameter for Cameca SU-30 WDS systems. XFlash 3001 SDD EDS has been operated under 15 kV accelerating voltage, 15 nA probe current. Counting times in the WDS systems were 10 s for elemental peaks and 10 s for backgrounds. In order to minimise the migration effect of alkalis, Na and K were analysed first in the WDS systems. The diffracting crystals used and the theoretical peak positions for WDS systems are shown in Table 1.

3. Elemental counting

WDS system is based on the collection of the distinct wavelength of the elemental characteristic X-rays by various diffracting crystals. The X-rays resulting from incident beam are diffracted by analyzing crystals (TAP, PET, LIF) and counted using gas-flow and sealed proportional detectors. Elemental counting in WDS is operated element by element. Besides, total X-ray spectrum, rather than the element-by-element counting, is recorded in EDS system. The difference of the elemental counts between WDS and EDS is slightly lower for silica poor minerals (5324 c/s in WDS, 4468 c/s in EDS), and become important for silica rich minerals (for the quartz mineral: 15,113 c/s in WDS, 11,721 in EDS), but this difference does not dramatically change the results. Although, the elemental count per second, which is not an important parameter for EDS system, is higher in WDS system, the total count of the elements, a function of acquisition time, is higher in EDS system. For the same quartz mineral, the total elemental count of silica is 151,130 in WDS and 293,033 in EDS.

4. Mineral analyses

A mineral can be described as a naturally occurring, solid, homogenous, inorganic substance, which has a well-defined crystal structure and a chemical composition. Classification of mineral species is based on the anion groups that they contain in their crystal structure. More than 95% of the rocks in the solid earth are made up from silicates, the largest and the most important group of rock-forming minerals. Silicates are natural compounds of Si and O, whose proportions define the silicate anion, and one or more metals.

Chemical analyses for minerals are commonly reported in terms of oxides of the elements, although oxygen is dominantly calculated stochiometrically. A traditional way to express the chemical composition as such as this would likely to mask evident relationships between elemental concentrations. In order to ease the interpretation and reveal the elemental