doi: 10.1017/S1431927609096007
Microsc Microanal 15(Suppl 2), 2009

Prospects for single standard quantitative analysis with SDD

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For concentrations > 5 wt% and x-ray line energies > 0.93keV, Newbury [1] found 95% of relative errors within +/- 25% for standardless quantitative analysis from two unnamed commercial systems using Si(Li) detectors. No elements below Z=11 were included and oxygen concentrations were calculated for minerals by stoichiometry. Silicon drift detectors (SDD) are now an attractive alternative to Si(Li) and Burgess et al [2] used Newbury's protocol for testing a commercial SDD-based system and showed 95% of relative errors were within +/- 10%. Both studies used normalisation to force the total to 100% which requires the operator to know all the elements present in the sample and also x-ray lines must be excited for all elements. Normalised results only provide corroboration for expected concentrations and give no indication of gross errors caused by missing or incorrect element identifications. If standards are used, normalisation is not necessary and independent estimates of concentration can be made for each element; if the analytical total is close to 100%, this provides an extremely useful indication that results are valid. The spectrometer efficiency should remain stable with time so that, after a one-off calibration using standards for every element under the same conditions, only a single standard measurement is needed to determine the intensities for all other standards at this condition. This one-off calibration using standards is still costly for the operator and a "factory default" calibration can be used on the assumption that all manufactured detectors will behave the same. When new detectors are developed, the factory default calibration needs to be adjusted by making assumptions about the change in detector efficiency. Fig.1 shows results from a set of analyses performed using an INCAx-act SDD and factory defaults in INCA Energy software suite 17b. The left hand histogram in Fig.1 shows the relative errors for a set of known reference materials using the same "standardless" protocol used in ref.[1], This confirms that standardless analysis with the SDD is capable of delivering results with errors < 10% and corroborates the conclusions of ref.[2]. However, many investigations involve concentrations below 5%, light elements such as oxygen and fluorine are not always combined stoichiometrically with heavier elements and an un-normalised total provides valuable information so a more exacting test is needed. When a single reference cobalt standard was used to obtain un-normalised results on the same system for elements >1% and with no stoichiometry assumptions, the histogram on the right of fig.1 shows a much wider spread and bias on the relative errors. This demonstrates that the assumptions about detector efficiency were not accurate enough so a new approach was taken to improve future "factory defaults". A direct measurement of efficiency vs energy was made using the Bessy II synchrotron [3] for a particular Oxford Instruments Si(Li) detector that was subsequently treated as a "gold standard" reference detector (6400GS). A set of detector parameters was deduced, consistent with the manufacturing process, which predicted a theoretical absorption behaviour matching the measured efficiency. 6400GS was mounted on an SEM with a special tilt stage and take-off-angle was determined to within 0.5 degrees. A large series of measurements on reference standards were taken under conditions of stable beam current and spectrum synthesis [4] was used to expose potential outliers. This provided a new analysis calibration consistent with the measured 6400GS efficiency curve. Using intimate knowledge of the manufacturing processes employed for each type of detector, the relative efficiency of an INCAx-act SDD was calculated relative to the 6400GS Si(Li) and used to generate a new efficiency curve for the INCAx-act SDD. The new

efficiency curve and analysis calibration were then used to repeat the tests using the INCAx-act SDD. The results in Fig.2 show that the new factory defaults and efficiency file reduce the errors for conventional standardless analysis. More importantly, the bias and spread for the un-normalised analyses using a single Co standard are considerably improved and are comparable to the accuracies expected for conventional microprobe analysis [1]. Since elements such as O and F are measured directly and an analysis total is available, this method is particularly useful for analyses at low kV where not all elements emit x-rays. Work is in progress to extend the approach using 5kV data.

References

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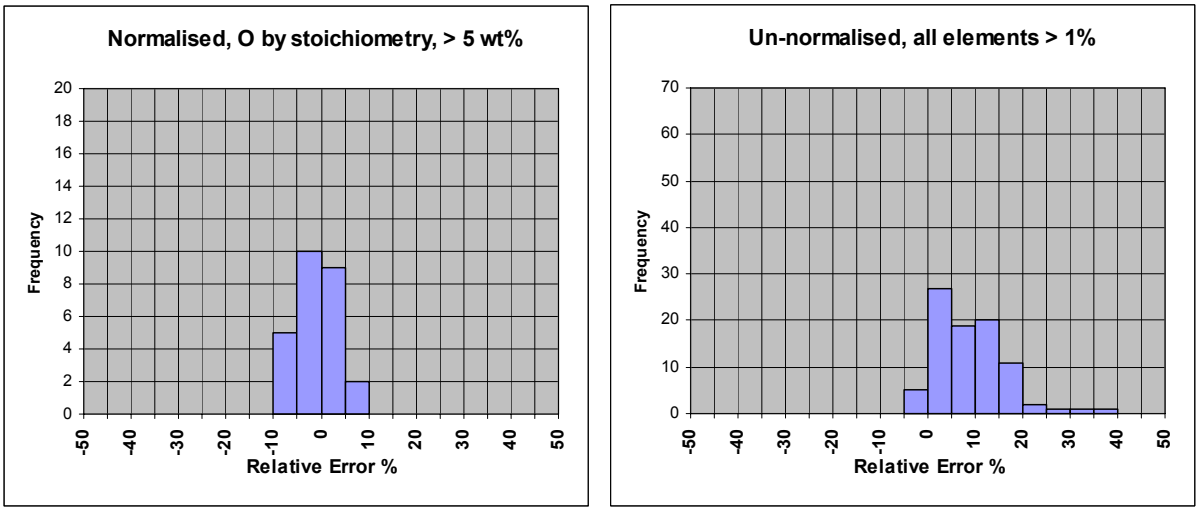

Fig.1. Histograms for 20kV analysis, 35deg take-off-angle, factory defaults for INCAx-act SDD

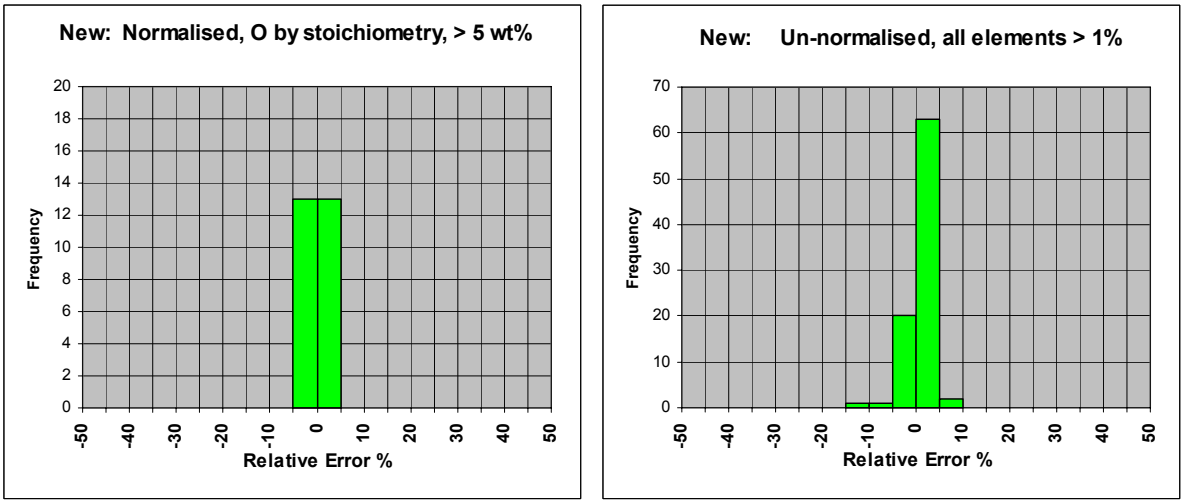

Fig.2. Same conditions as Fig.1 with new efficiency calibration derived from "gold standard" detector. Un-normalised analysis achieved using a single cobalt standard as reference.

https://doi.org/10.1017/S1431927609096007 Published online by Cambridge University Press