Non-destructive Spectrometric Determination of Trace Element Concentration of Rubidium, Strontium, Yttrium Zirconium and Niobium in Ceramics

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A simple X-ray spectrometric method for the simultaneous quantitative determination of the trace elements Rb, Sr, Y, Zr and Nb in Chinese porcelains is described. The results of the analysis show that Jingdezhen porcelains from later Ming to the Republic period have concentrations of these elements lying within narrow ranges whereas modern (after World War II) porcelains, whether Jingdezhen or otherwise, have concentrations of one or more of these elements lying outside these ranges. This offers a simple nondestructive method of detecting modern fakes.

Introduction

The elemental analysis of Chinese porcelains has to be non-destructive for obvious reasons, and this restricts the techniques available for such an analysis. Recently, X-ray spectrometric studies of Chinese porcelains [1–8] of the Ming (1368–1644) and Qing (1644–1911) dynasties, the Republic (1912–1939) period and after World War II times gave encouraging results on the attribution and dating of Chinese porcelains and also on the identification of modern fakes. However, quantitative elemental determination has so far only been done on barium [6].

In this study we used a simplified, rapid X-ray spectrometric method to obtain quantitative values of the trace elements Rb, Sr, Y, Zr and Nb in Chinese porcelains. Briefly, it makes use of the calibration curve [9, 10] on an ln [Intensity (cps)/concentration (%)] vs. ln [Energy (keV)] plot for the elements from Rb to Nb. Using such a calibration curve, we could easily obtain quantitative values of the concentrations of an element by simply measuring its intensity under the same geometrical conditions.

There is a special reason for studying the elements from Rb to Nb. It has been shown [2] that porcelains made in Jingdezhen, since early Ming the almost exclusive place of porcelain manufacture in China because of the nearby occurrence of high quality feldspar and kaolin, have a characteristic feature in the rubidium-strontium-zirconium-niobium K-lines region which is quite different from that of porcelains made elsewhere, whether inside or outside China. However, our previous work was qualitative and yttrium could not be studied as its peak is immersed in the Rb K_β peak. In this investigation, we analysed 122 pieces of Chinese porcelains made in Jingdezhen from late Ming up to 1983, including a number of non-Jingdezhen porcelains. Concentrations from a few ppm for niobium up to a few hundred ppm for rubidium are presented and discussed.

Experimental

The X-ray spectrometer used was the standard energy-dispersive XRF system, consisting of a Si(Li) detector with the associated electronics and multichannel analyzer, which was coupled to a computer for storage and analysis. The exciter was an annular ^{109}Cd source. All spectra were analysed by the commercial program known as AXIL (Analysis of X-ray spectra by Iterative Least-squares fitting).

The geometry to be chosen as to the annular source, the position of the sample and the detector has been explained in [11].

To obtain the calibration curve shown in Fig. 1, a piece of porcelain was ground to fine powder with an agate pulverizer. Five thick pellets containing known amounts of Rb, Sr, Y, Zr and Nb, respectively, were made at a pressure of 20 tons/inch^2. Mixing for homogeneity was done with the agate pulverizer for several hours. The pellets had a diameter of 30 mm and around 4 mm in thickness, which can be considered to be infinitely thick [8].

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It is well-known that SiO_2 and Al_2O_3 are the main constituents (about 95%) of porcelain samples, with Na_2O, K_2O, CaO and Fe_2O_3 as minor constituents. A recent wet-chemistry study [12] showed little variation in these constituents. We made a preliminary study to find out possible errors due to extreme changes in the composition of porcelain samples. For this, thick pellets were made from mixtures of pure SiO_2, Al_2O_3, Fe_2O_3, $CaCO_3$ and K_2CO_3. Extreme variations of the main constituents were made: from about 10% Al_2O_3 and 85% SiO_2 to 45% Al_2O_3 and 40% SiO_2. We found that such an extreme variation in the matrix would result in a change of about 8% in the measured concentrations, which is normally acceptable for sample like porcelains.

Results and Discussion

All porcelain samples were exposed on plain regions which were not decorated and were as flat as possible. The regions chosen must also be at least 3 mm thick, and therefore this rules out egg-shell porcelains and miniature vases. We present the results in Figures 2–6. For good statistics, the samples were exposed for at least 10 000 s with many overnight exposures of 50 000 s. The statistical errors at 2σ are roughly 1% for Rb, 2% for Sr, 3% for Zr and 8% for Y and Nb for samples exposed for 10 000 s. By using stronger sources the exposure times can be reduced.

From the figures we conclude that the elemental concentrations of Rb to Nb for Jingdezhen porcelains from late Ming to the Republic period lie within narrow ranges:

$$200\ \text{ppm} \leqslant \text{Rb} \leqslant 430\ \text{ppm},$$
$$60\ \text{ppm} \leqslant \text{Sr} \leqslant 140\ \text{ppm},$$
$$10\ \text{ppm} \leqslant \text{Y} \leqslant 23\ \text{ppm},$$
$$35\ \text{ppm} \leqslant \text{Zr} \leqslant 55\ \text{ppm},$$
$$11\ \text{ppm} \leqslant \text{Nb} \leqslant 20\ \text{ppm}.$$

Non-Jingdezhen porcelains, in general, are quite different. Moreover, many modern Jingdezhen porcelains have one or more elements lying outside the range of concentration values given above. This offers a simple and the only non-destructive method for detecting modern fakes, especially those of imperial quality when even porcelain experts could be helpless. We have examined a reasonably large number of such porcelains from various collectors, the price they paid

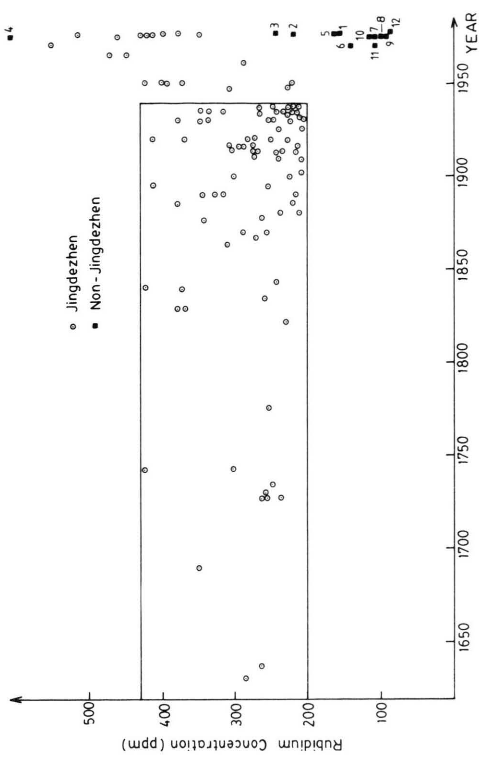

Fig. 2

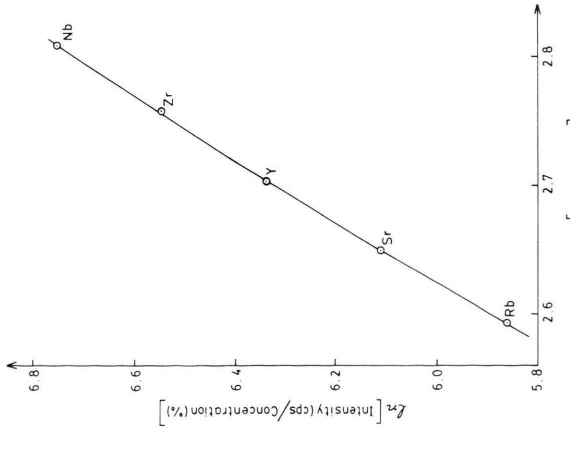

Fig. 1. ln [Intensity (cps)/Concentration (%)] vs ln [Energy (keV)]

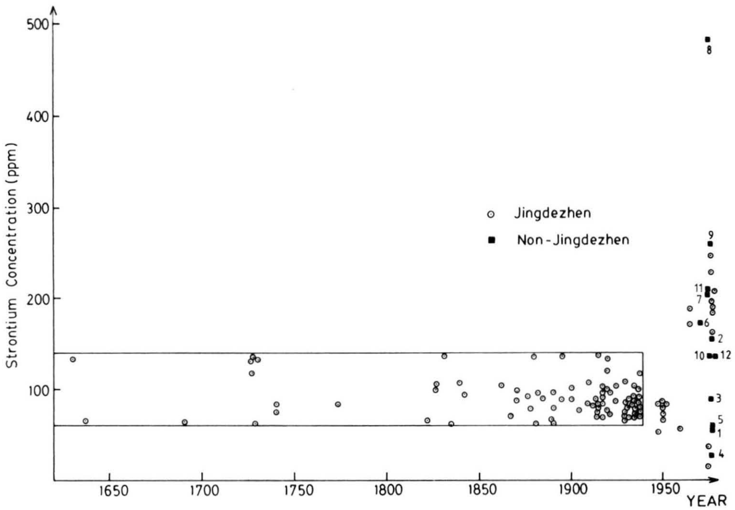

Fig. 3

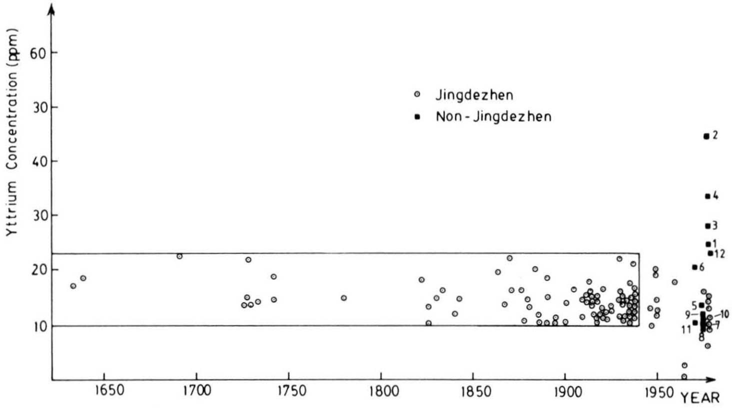

Fig. 4

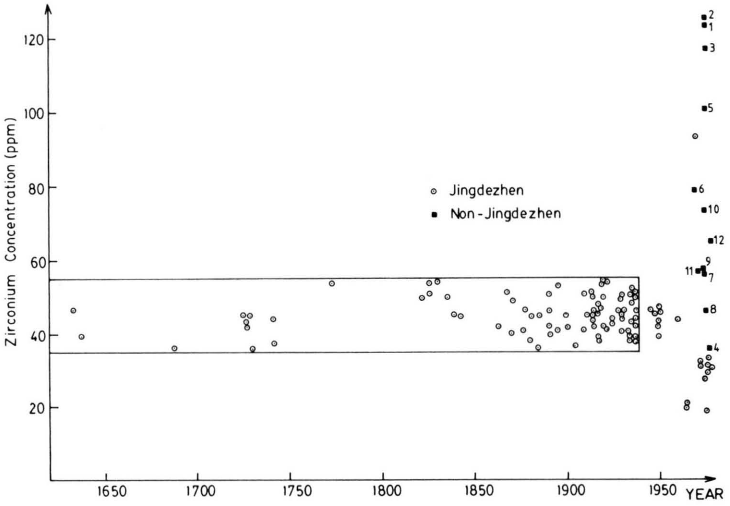

Fig. 5

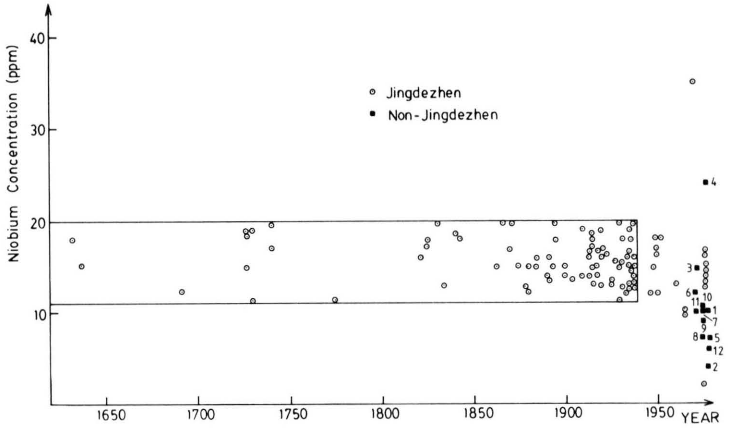

Fig. 6

Figs. 2–6. Concentrations of Rubidium, Strontium, Yttrium, Zirconium and Niobium vs. date of manufacture. The non-Jingdezhen pieces are numbered.

for such "antique" pieces varying from US$ 150 for a Qing piece to US$ 150 000 for a Ming piece, and which we showed to be fakes from Taiwan, Thailand, Indonesia or even from Jingdezhen itself.

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