ELSEVIER

Nuclear Instruments and Methods in Physics Research B 95 (1995) 389–392

NIM B
Beam Interactions with Materials & Atoms

Galileo's writings: chronology by PIXE

L. Giuntini [a], F. Lucarelli [b], P.A. Mandò [b], W. Hooper [c,d], P.H. Barker [e,f,*]

[a] *Istituto Nazionale di Fisica Nucleare, Sezione di Firenze, Firenze, Italy*
[b] *Dipartimento di Fisica, Università di Firenze, Firenze, Italy*
[c] *Istituto e Museo di Storia della Scienza, Firenze, Italy*
[d] *Department of the History and Philosophy of Science, Indiana University, Bloomington, Indiana, USA*
[e] *Istituto Nazionale di Fisica Nucleare, Sezione di Firenze, Firenze, Italy*
[f] *Physics Department, Auckland University, Auckland, New Zealand*

Received 16 May 1994; revised form received 4 November 1994

Abstract

PIXE studies of Galileo's manuscripts have been initiated with the aim of establishing element profiles of the inks used, so that, by associating the profiles of undated works with those of dated documents, the development of his ideas may be better understood. Some success has been achieved, and a particular example is discussed.

1. Introduction

The technique of PIXE (particle induced X-ray emission), in which characteristic X-rays, emitted by samples under bombardment typically from a 2–3 MeV proton beam, are studied to gain information on surface elemental composition, is well established in many areas [1]. In particular for the analysis of materials in ancient documents, extensive work, starting in 1984, has been performed by the group at Davis, California, who studied the inks employed in a copy of the Gutenberg Bible [2,3] and in the Vinland map [4], which showed the great potential of using PIXE with external millibeams in problems related to reconstruction of printing techniques, authenticity, etc. Also the Florence group has now considerable experience in the examination of the inks and paints used in ancient manuscripts and in the interpretation of the results [5,6], which it seems especially appropriate to proceed to apply to the works of Galileo, since a major repository of his written manuscripts is in the Biblioteca Nazionale, in Florence, which holds the Manoscritti Galileiani (Ms. Gal). It should be added that an analysis of Galilean writings has a particular appeal to a group of experimental physicists working in Florence, since Galileo was closely asociated with Florence during his lifetime and a large fraction of his most significant works was composed here – in particular the "Dialogues on two new sciences" which constitutes the foundation of the modern experimental method and of modern mechanics.

Working at the end of the sixteenth century and the beginning of the seventeenth, Galileo used hand-made inks and folio sheets of paper composed of inhomogeneous, pre-industrial materials in varying amounts. A substantial proportion of the surviving folios relating to his scientific work were not dated by him (especially the fragmentary documents on motion in Ms. Gal. volume 72), thus posing problems for subsequent scholars who wished to understand the development of his thought. However, there is a quantity of individual letters which are dated (Ms. Gal. 14 and 86), and, in addition, there is an "accounts book" (Ms. Gal. 26), in which Galileo recorded the details, including the date, of transactions of his scientific instruments business, his tutoring work, and his domestic affairs, so that if the folios can be associated in time with the dated works, some progress might be made. Ultimately the accounts book, which has frequent entries but which is physically less straightforward to deal with, will provide a reasonably fine-scale reference source, but the present work is restricted to some of the letters in Galileo's familiar correspondence in Ms Gal. volume 14.

Previous attempts to date the notes on motion in Ms. Gal. 72 have made use of textual evidence such as Galileo's language and references (see for example Ref. [7]), and of certain kinds of physical evidence like the watermarks on the papers [8]. The textual evidence has been regarded as decisive for only one folio – ff128 – of the more than 190 in Ms. Gal. 72, and watermarks normally allow localisation to only a very limited degree.

* Corresponding author, tel. +64 9 373 7599, ext. 8836, fax +64 9 3737445, E-mail: phb@phyvc.auckland.ac.nz.

SSDI 0168-583X(94)00538-9

For PIXE to be successful in dating a manuscript by correlating the elemental composition of its ink with that of one or more letters, certain minimum requirements need to be met. Firstly, the inks should contain elements to which PIXE is sensitive, for purely organic inks could have been used. Secondly, one must prove the very possibility of defining "periods", i.e. time intervals during which the same ink source, and only that source, was used. That Galileo is known not to have moved very often, together with the cost and availability of ink at the time, argue in favour of this. The periods should not have been too long to preclude the establishing of a sufficiently fine chronology; but they should also have been long enough to avoid an excessively large number of ink "profiles" in the database, which would result in a more difficult matching to those of the undated documents. Indeed, we recall that a certain amount of scatter in the PIXE profiles has been seen even in samples from the same document [5,6], due to the inhomogeneities inherent in the suspensory nature of the ink. In summary, the PIXE profiles of the inks should be sufficiently consistent within the same period, but sufficiently different over letters from different periods, that there should be no ambiguity in assigning an undated proposition to a given period. Establishing these criteria is the main feature of this report.

2. Method

The experimental procedure in the Florence PIXE laboratory has been described several times, (see e.g. Ref. [5]), and will be discussed only briefly here. The proton beam from the University of Florence 3 MV Van de Graaff accelerator is collimated to 0.15 mm diameter and then emerges through a thin Kapton foil into the atmosphere, where, after travelling roughly 1 cm, it strikes the sample under investigation perpendicularly. The X-rays emitted are detected in two Si(Li) crystals, oriented at about 135° to the beam axis, whose absorbers and whose distances from the sample are chosen so that one is primarily sensitive to elements lighter than, say Z around 25 and the other to elements heavier. The volume surrounding both the track of the proton beam outside the vacuum and from the bombardment point to the low energy X-ray detector is flushed continuously with helium, to minimise the production of the argon K X-ray from the atmosphere and to reduce the absorption of soft X-rays. The intensity of the proton beam is monitored by rotating a carbon arm with a thin nickel surface layer regularly through the beam and measuring the nickel K X-rays. In all, separate X-ray spectra from the sample and from the nickel are recorded for each detector, and in addition spectra are taken of those pulses affected by pile-up in the electronic systems.

For the letters, the folios had been bound in a book, and the page under scrutiny was carefully held perpendicular to the beam in a stand [5,6]. The intended point of impact of the beam could be seen and adjusted using the image of the spot of a He–Ne laser which shone down the same path as the protons would traverse. This enabled the ~ 0.2 mm diameter impact area to be centred on a small portion of a particular letter in a word. A proton exposure typically took 2–3 min with an intensity of only 100–200 pA on target to avoid any damage. This is a problem of the utmost importance in any analysis of precious objects, in particular documents, by ion beams. In our experience over the last seven years, we can say that, under the conditions under which we now operate, we have never detected visible damage in the examined documents. The key point is, of course, the use of a cooling flow on the bombarded spot, as shown also in the theoretical estimates by McColm [9]. In this connection, the helium flush we use in our setup is essential, not only for the detection of low-Z elements, but also as a cooling agent. These measurements could never be performed in vacuum! As a further precaution, the whole process was continuously monitored anyway using a video camera.

Of the 101 folios with relevant ink samples which are bound in the Ms. Gal. 14, 17 have been studied, mainly covering the period 1605–1609, with one example from each of 1600, 1617 and 1636. For each, spectra for generally three ink and two blank, (i.e. paper) positions were taken. At the beginning and end of every session the detector total efficiencies were determined using thin target standards of known areal density.

The X-ray spectra were analysed in an uncomplicated manner to give peak areas, and these were converted into absolute elemental areal densities using the calibrations, after small corrections for pile-up. This process essentially assumes a thin target with no self-absorption of the emerging X-rays, which is somewhat doubtful as the ink is certainly thicker at a point where the pen had just been charged, and it will in any case have soaked into the paper. However, the critical information for discrimination was provided by elements from potassium upwards, for which experience has shown self-absorption is not a serious problem, and the final data is presented as ratios of elemental densities, which further mitigates the effect.

3. Results

The profiles for the 17 letters from Ms. Gal. 14 are shown in Fig. 1. Each is in terms of the mass concentrations of potassium, iron, copper, zinc, lead and nickel with the sum normalised to 100%. None of these elements was present in significant quantities in the paper, and therefore their attribution to the ink is unambiguous, but this was not true for those in the range sodium to sulphur, and also for calcium, which is why these have not been used. Eight folios were sampled twice and the rest three times, and the self-consistency between points in the same folio seems quite acceptable, at least from the point of view of pattern

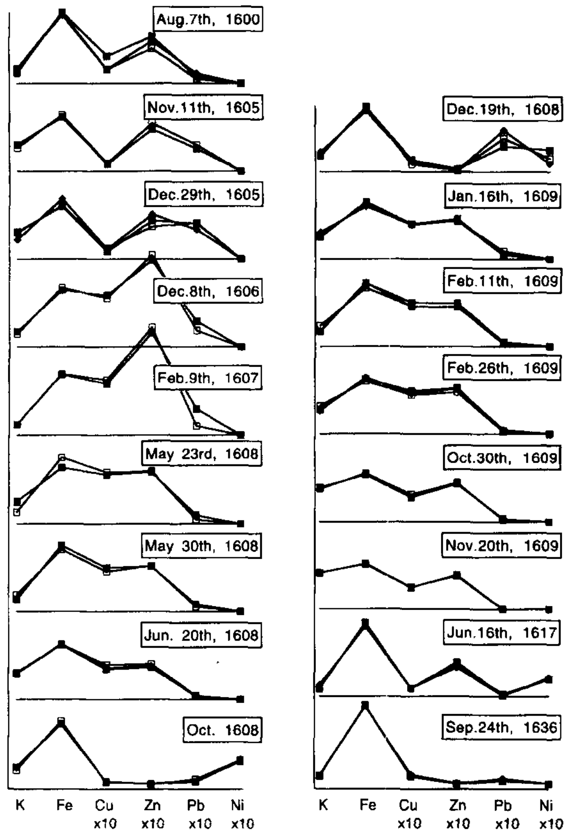

Fig. 1. Element profiles for the inks from seventeen dated letters from Manoscritti Galileiani, vol. 14.

recognition. In addition, one can recognise profiles which continue from one letter to another, for instance the sequence Dec. 8th, 1606 – Feb. 9th, 1607; that of May 23rd – May 30th, 1608, possibly extending to June 20th, (although this contains significantly larger amounts of K); that of Jan. 16th – Feb. 11th – Feb. 26th, 1609 and the sequence Oct. 30th – Nov. 20th, 1609. Also the profiles of the letters dated Nov. 11th and Dec. 29th, 1605 might be considered sufficiently similar to define a period. Assigning absolute errors to the data points in the profiles would be somewhat problematic. Since the abundances are normalised to 100%, and potassium and iron are the major components, their values are in any case strongly correlated. However, some feel for the data can be gained by quoting the statistical accuracy of the peak areas of the different lines. These were: below 5% for iron and potassium, 5% to 10% for copper and zinc, and for nickel when it was present, and 10%, or occasionally up to 30%, for lead. But, as may be seen, the variation from spot to spot on a particular piece of writing is probably the largest factor in deciding whether it can be said to exhibit a characteristic "pattern".

4. A particular case

Profiles from ff163 and ff164 of Ms. Gal. volume 72 are shown in Fig. 2. Each folio contains three propositions relating to Galileo's developing thoughts about projectile motion, and there has been much discussion amongst scholars as to when they may have been written, and even

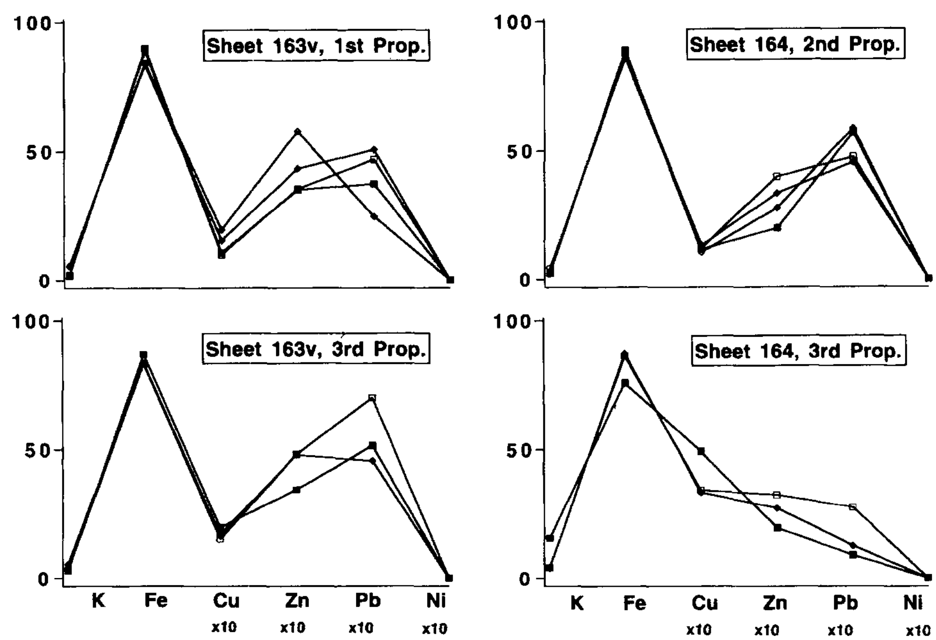

Fig. 2. Element profiles from two undated folios from Manoscritti Galileiani, vol. 72. (See text).

a suggestion [10], that proposition three of ff164 was written a good deal later than the others. Of course the preliminary data-base of dates and profiles discussed in the previous section is not yet complete enough to allow an unambiguous dating of the writings, but it is fairly evident that whereas the profiles of ff163v 1st prop., ff163v 3rd prop. and ff164 2nd prop. seem to be quite similar, that of ff164 3rd prop. does indeed seem to be different, principally in the amounts of copper and lead. One also notes however the somewhat unsatisfactory scatter in the several profiles taken for each proposition, and this aspect will have to be examined further.

5. Conclusion

A relatively unambiguous profile of the inks used in some of Galileo's dated manuscripts has been adduced by external beam PIXE, in a procedure which is convenient and which causes no deterioration of the sample. The technique has been used to provide strong support for asserting that a particular and significant portion of an undated folio was written at a different time to the rest of the sheet. We hope to go on to provide a detailed data-base for a chronology of Galileo's writings and to consider some undated manuscripts of particular interest.

Acknowledgements

We would like to thank the staff of the 3 MV Van de Graaff laboratory at the University of Florence, particularly A. Pecchioli, for their strong support. Dr I. Truci of the Biblioteca Nazionale was always extremely helpful and attentive and took an enlivening interest in the investigations. W. Hooper acknowledges the support of the Istituto e Museo di Storia della Scienza, and particularly of the Director, Prof. P. Galluzzi. P.H. Barker is very grateful for the warm support afforded by colleagues in the Dipartimento di Fisica, Università di Firenze, and P.A. Mandò was supported by a "60%" contribution from the Università di Firenze, by the "40%" project "Uso piccoli acceleratori" of the MURST, and by a contribution from Committee XV of CNR.

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