INDIRECT CHRONOLOGY OF ANCIENT DOCUMENTS THROUGH THE ANALYSIS OF THEIR INKS BY EXTERNAL PIXE

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As is well known, PIXE (Particle Induced X ray Emission) is a nuclear technique for a very fast, sensitive and quantitative *elemental analysis;* all elements with $Z > 10$ (i.e. from Na included) are *simultaneously* detectable, and *micro*-analysis is also possible. The main drawbacks are that no information can be obtained on *organic* components, nor on the *chemical form* in which the detected elements are bound.

The working principle of the technique is illustrated in figure 1. A proton beam from an accelerator is used to bombard a "target", i.e. an object, the composition of which is to be investigated. The proton bombardment causes inner-shell ionisations of the atoms in the material of the target. Following these ionisations, a prompt rearrangement of the atomic electrons takes place, with an outer electron performing a transition and filling the hole created by proton-induced ionisation. The energy difference between the initial and the final position of the electron is released and this may occur through the creation of an X ray, having an energy just equal to that difference. Since electron energies in the various orbits are characteristic of each given atomic species, the energies of the emitted X rays also depend on the element from which

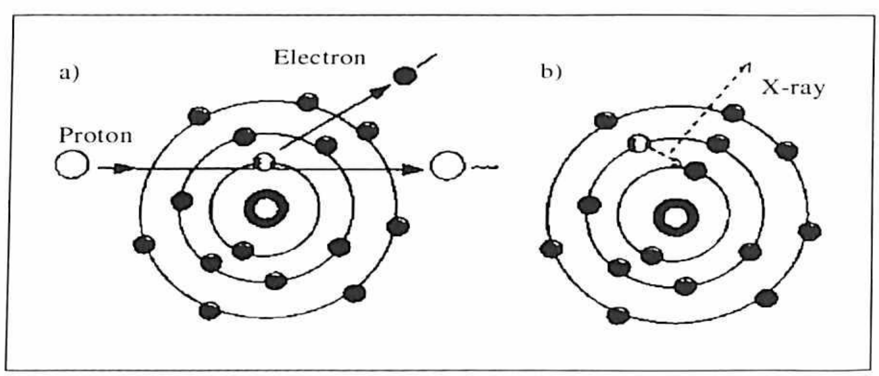

Figure 1. Schematics of a process of Proton-Induced X ray Emission.

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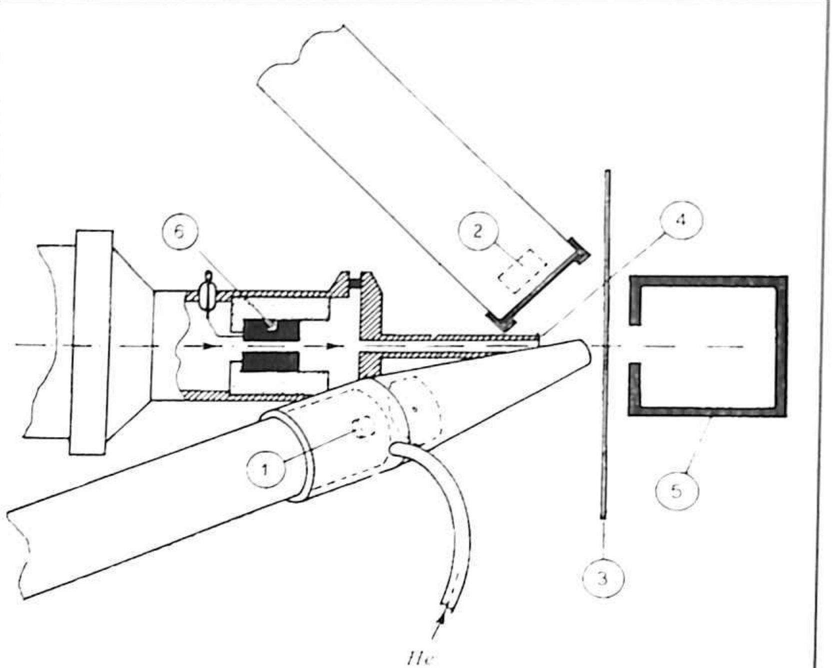

1,2) X ray detectors 3) sample to analyse

4) beam exit window 5) Faraday cup

6) graphite collimator

Figure 2. The set-up for external beam measurements at the 3 MV Van de Graaff accelerator of Istituto Nazionale di Fisica Nucleare, in Florence.

they originate: therefore, the detection and energy classification of X rays leads to identifying the elements that are present in the target.

A frequently used set-up for PIXE measurements on objects of relevance to the Cultural Heritage makes use of an "external beam". This means that the proton beam is allowed to exit to atmosphere from the vacuum lines of the accelerator, through a thin window where the beam particles undergo only a small energy loss. The object to be analysed is in this case placed just after the exit window and the problems connected with its placing under vacuum are avoided. This way, a number of substantial advantages are obtained:

- ease of handling and moving the target;
- possibility of analysis of objects of whichever size;
- no need of picking up of samples;
- negligible electric charging;
- negligible heating, thus no thermal damage;
- no dehydration problems.

Figure 2 shows the external beam set-up for PIXE measurements, at the accelerator in Florence. The simultaneous use of two X ray detectors has further important advantages, in that it makes it possible to extend the range of detected elements.

Let's come to the specific applications I wish to describe here: the analysis of ancient inks. Two classes of inks might *a priori* be expected: carbon-black inks (undetected by PIXE, due to the low-Z limitation mentioned above), and the so-called metallo-gallic inks. The latter are mixtures of vitriols (sulphates of iron or of other metals, often containing several of them in detectable quantities) with tannins (vegetal essences from gall-nuts). They are easily characterised in a quantitative way by PIXE, with no need of particularly sophisticated set-ups. Indeed, the large enough ink mark size implies no need of microbeams; the high sensitivity of PIXE makes the use of very low beam currents (< 100 pA) possible, minimising the risk of damage; the very short times of a single analysis make extended "sampling" possible over many different spots of a given writing. Probably, no other competitive non-destructive techniques exist for the analysis of inks.

In the PIXE analysis of metallo-gallic inks, the most useful characterising feature of their composition are the ratios among the quantities of the various metals. Indeed, the relative amounts of Mn, Fe, Ni, Cu, Zn, Pb may largely vary from ink to ink, thus differentiating among different inks, and the ratios among these metals, as directly deduced by X ray intensities in the PIXE spectra, are little affected by the "matrix" effects[2]. Figure 3 figure shows examples of PIXE spectra taken from three inks of different composition: even the non-expert can immediately realise that a discrimination can be easily performed.

An example of how the detection of ink composition differences may lead to useful results for the historians is provided by the analysis of inks in Galileo's hand-written notes on the problems of motion. Some very short introduction of the problem, just from the point of view of the History of Science, must be preliminarily given.

Galileo's ideas about "natural motion" (i.e. the motion of falling bodies under the action of gravity) evolved during his life (1564-1642) from traditional belongings to the modern statements of the *Discorsi e Dimostrazioni Matematiche intorno a due Nuove Scienze* (1638). The path through which Galileo reached this final settlement is witnessed by almost 200 hand-written folios containing propositions, sketches of drawings, notes of experiments and reckonings. In XIX century, these folios have been bound in a volume, Ms.Gal.72, now kept in the Biblioteca Nazionale of Florence. The hand-written notes are unfortunately not dated, but to the highest evidence many of them have been written at successive times, with corrections, erasures and additions: thus, the problem of a chronological ordering of their content is really complex. On the other hand, a chronological reconstruction is of great importance for the History

[2] i.e. the alteration of intensity ratios produced by the beam energy loss and by X ray self-absorption within the "matrix", namely the paper in which the ink is absorbed.

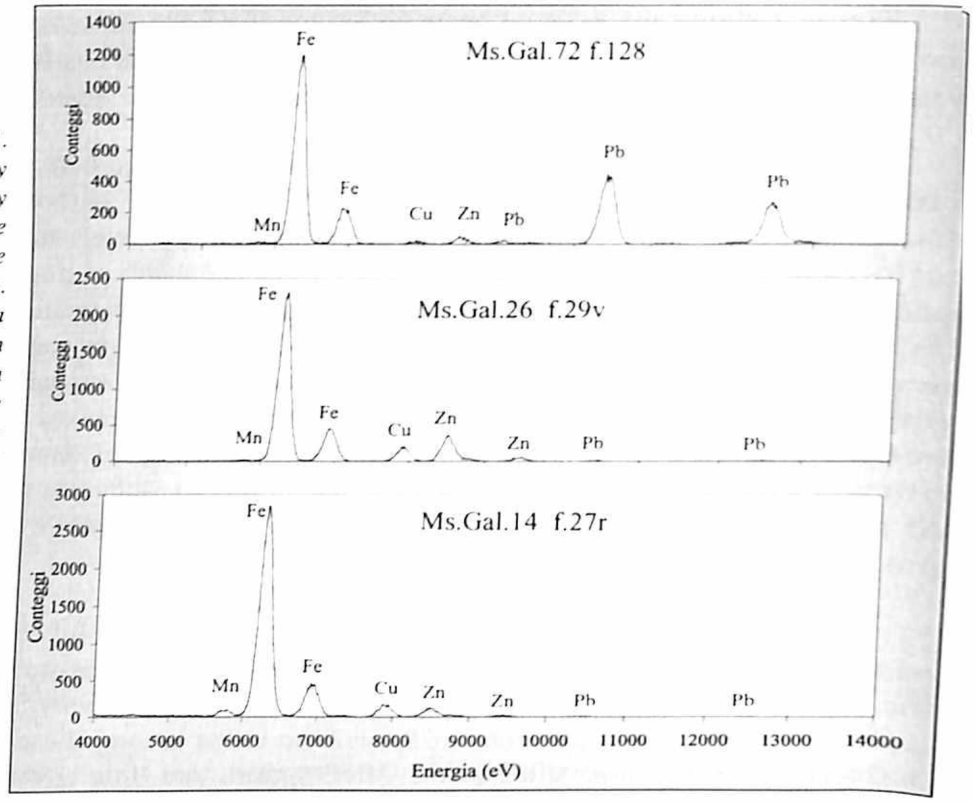

Figure 3. Examples of X ray spectra obtained by bombarding three spots of inks in three different documents. The presence of a peak at a given energy is an indication of the presence of the corresponding element (shown by its chemical symbol). The height of the peak is related to the abundance of that element in the bombarded material. As is easily seen, the difference from one ink to another may be very large.

of Science: it helps reconstructing the evolution of Galileo's way of thinking, correlating it to the events of his life and to the parallel development of scientific investigations in the European cultural environment at those times.

Examples of problems addressed by the study of Galileo's hand-written notes are the following:

- when did Galileo fully understand the correct quantitative relationships between space, time and velocity in the natural motion, the independence of simultaneous motions and the rules governing the parabolic motion of projectiles?
- did he actually perform certain experiments, which he later described in the *"Discorsi"*
- when did he correct the errors through which he himself passed?

To provide some contribution to the chronological reconstruction of the notes, a project, to which we refer by the name "Galileo-PIXE", started some years ago. It is a collaboration among various groups and Institutions, including physicists, historians of Science and librarians. The idea is to indirectly "date" the documents by PIXE measurements of their ink composition: "relative" chronology can be obtained by comparing inks in different folios or in different parts within the same folio, and even a reconstruction of "absolute" chronology can be envisaged by comparing inks of the

undated documents to those in dated ones (letters, personal "agenda"), which luckily exist (see e.g. figure 4).

Of course, the criterion based on ink composition comparisons is not assumed to be the only one to chronologically assign the folios: lot of science-historical studies based on the contents of the folios themselves, and on documentary evidence, are currently being performed. However, in some cases serious controversies have arisen among historians of Science concerning specific points, and we hoped that the further criterion provided by ink composition might help solving some of these controversies.

A basic question however had to be preliminarily answered: is "dating the notes" through ink composition really plausible? *A priori*, we had good hopes for the following reasons:

- the ink composition at Galileo's times was surely "home made";
- as a consequence, it is a reasonable expectation that at least the quantitative ratios among ingredients vary from batch to batch;
- we expected that the "lifetime" of an ink batch was not too long nor too short.

To confirm these expectations, a PIXE analysis of inks in dated documents by Galileo was preliminarily undertaken. The results showed that:

- the used inks were metallo-gallic, therefore detected by PIXE (see the examples in figure 3, all taken from Galilean writings);
- the detected ink composition in documents written at short time intervals is quite similar;
- the detected ink composition varies from a "period" to another.

Figure 4. Two pages from the "book of expenses and incomes" of Galileo (Ms.Ga.26. Biblioteca Nazionale di Firenze).

From these results, we had then hopes that the ink composition in an undated document might be really useful in reconstructing its chronological position, and the Galileo-PIXE project could actually start.

So far (1999), about 600 ink spots have been analysed from 28 folios in *Ms.Gal.72*, and about 250 spots in inks of presumably known date (letters or personal agenda [*Ms.Gal.26*]). A few examples of results of some relevance are now presented.

ABSOLUTE DATES

A first result is the assignment of the date of f.128 of *Ms.Gal.72*. In this case, more than solving controversies, our aim was to increase the confidence in the validity of the PIXE-based approach to dating, by confirming a chronological assignment independently believed to be true on a documentary basis. This folio contains a demonstration by which Galileo reaches a correct conclusion about natural motion (the time-square

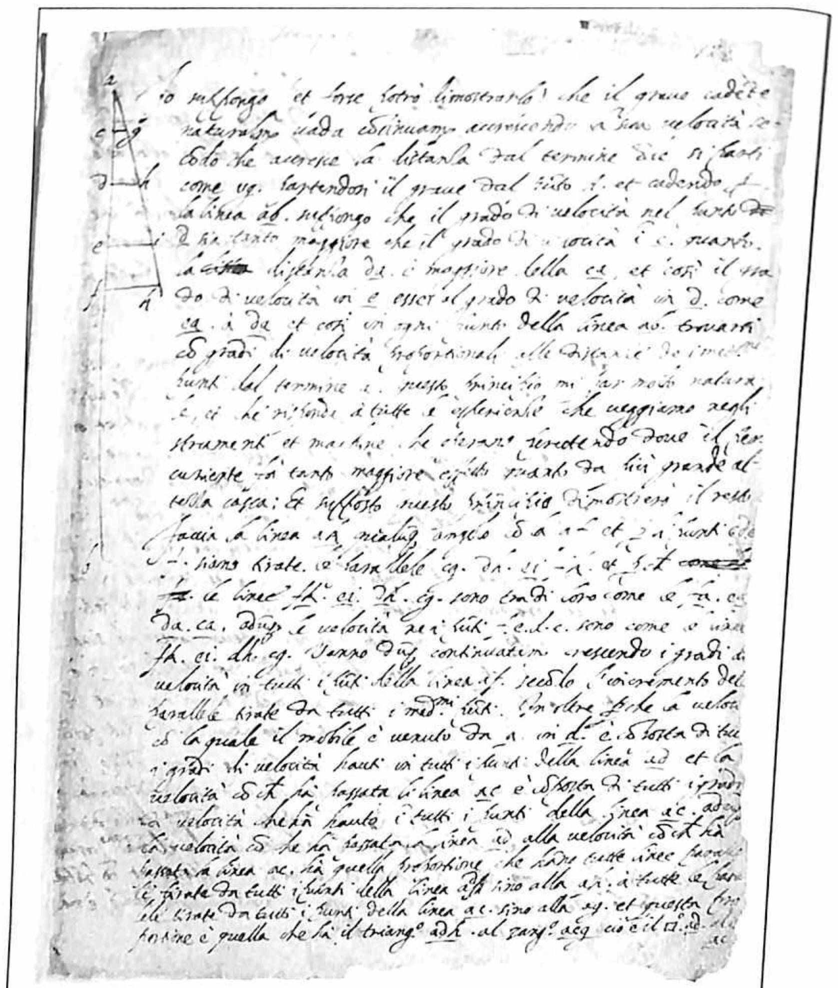

Figure 5. Folio 128v of Ms.Gal.72, Biblioteca Nazionale di Firenze.

dependence of distance) obtained however through a wrong statement (that velocities are proportional to distance rather than to time). There is a wide consensus that f.128 was written at the beginning of fall 1604, based on sound documentary evidence.

We have examined 15 ink spots in that folio. A very peculiar ink composition was detected: Pb is present with an abundance, which we never found in any other ink (letters or other undated documents by Galileo, nor in any other). We have also analysed a large number of dated writings, belonging to the period from 1603 to 1605. Inks of different compositions were found to be used during this period, and in particular in the documents dating from April 1604 to the first months of 1605, we detected an ink, which also shows unusually large quantities of lead. The quantity of lead is so unusually large in the two sets and only in them, that it may be considered a very characterising common feature by itself. Also the other discriminating elemental ratios (Cu/Fe and Cu/Zn) are similar and quite compatible between the two sets.

As a whole, the match between the two sets of ink data seems to be very stringent, confirming the dating of folio 128v to fall 1604.

COMPARATIVE DATING

This example deals with the third and fourth proposition of f.164v of *Ms.Gal.72*. The two propositions, as written by Galileo, are shown in figure 6.

The third proposition, in the form of a paradox, eventually states, quite correctly, that bodies accelerate to the same speed when they fall through the same height regardless of the inclinations of their paths. Although it does not consider the relation between velocities acquired at different heights, yet the ideas expressed in this proposition figure centrally in another discussion of the incorrect law of speeds (v proportional to s, see above). On the other hand, the fourth proposition explicitly gives the correct law of speeds (v proportional to the square root of s), so the question arises whether it was written in the same period as the third or was added at a later date. One of the pioneers in the studies on Galileo's notes on motion, S. Drake, argued that they were written together in 1607. Other historians of Science have suggested that the third

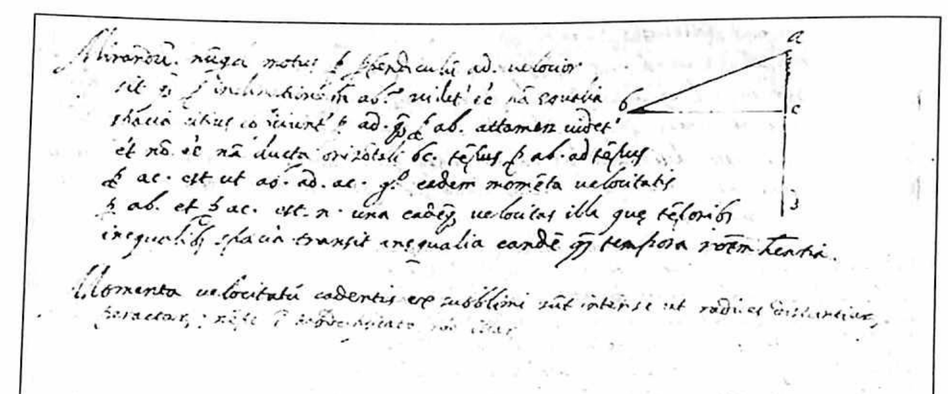

Figure 6. The third and fourth proposition in folio 164v, Ms.Gal.72.

proposition may have been written earlier, when the correct law of speeds had not yet been recognised, while the fourth was added later, when Galileo had verified the proportionality of speed to time (rather than space) in the natural motion.

From the ink composition data (figure 7), evidence is obtained for a clear-cut difference between the inks used in the two propositions, so that Drake's opinion seems to

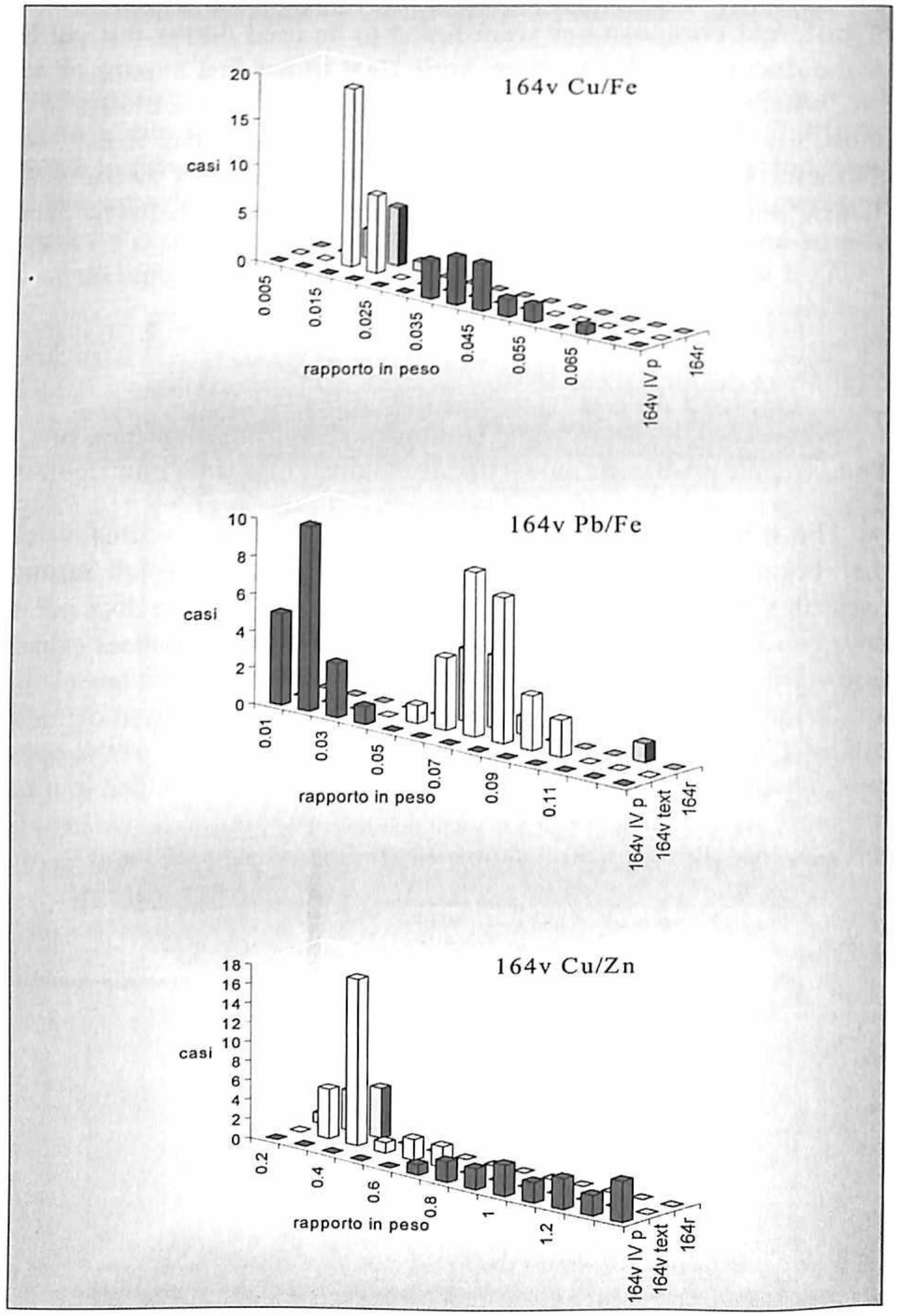

Figure 7. Distributions of the weight ratios measured for Cu/Fe, Pb/Fe and Cu/Zn in the examined spots of ink of the third and fourth proposition of f.164v. Also shown are the results from f.163r.

be wrong. This is shown by the summary of the results reported in the figure. In spite of the scattering of the data concerning the ratios of metals in the ink within each of the two propositions, the overall results unambiguously differentiate the two sets.

Finally, it had been also proposed that the third statement, if assumed to belong to the period of the wrong assumption on the law of speeds, had to be associated to the contents of another folio, f.163v, where the mistaken principle is explicitly stated. As is seen again from figure 7, the ink composition data reinforce such an association.

Another example concerns Folio 179v in *Ms.Gal.72*.

This is a folio with two "attachments", i.e. two smaller folios glued to its side, containing further statements each with a sort of "title". We will call these smaller folios attachment "a1" and "a2", just based on their position and not on any chronological hypothesis. The attachments partly seem to correct the ideas expressed in the propositions of the larger folio. This would imply a later date for their writing, but their content might simply improve, in the mind of Galileo, their understanding, in which case they might have also been written at the same time (between them and with the folio). The question then arises on which had been the actual sequence in which they were written. From an analysis of many spots in each of the *a priori* possibly different inks (various statements in the main folio, attachment "a1", its title, attachment "a2", its title), just

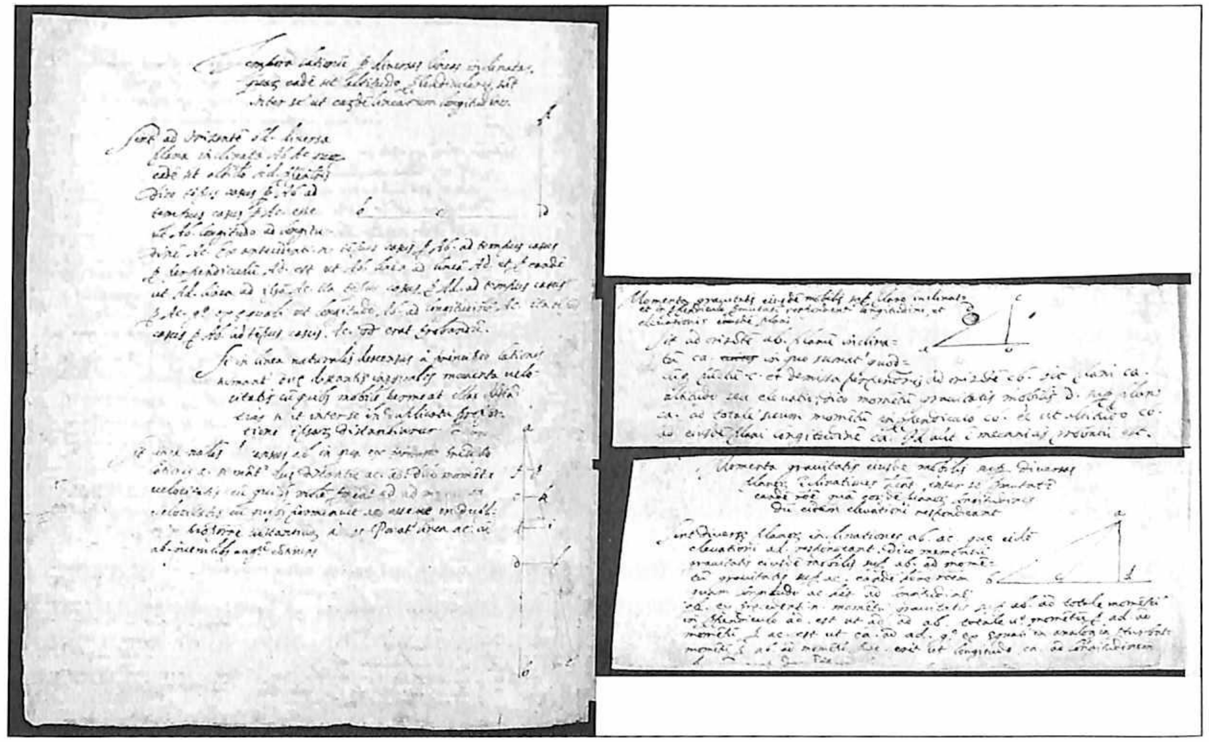

Figure 8. Folio 179v of Ms.Gal.72, with attachments "a1" (above) and "a2" (below).

two different inks came out to have been used in total. One of them is found on all parts of the main folio and on the text of attachment "a1". The other is found on the text and title of attachment "a2", and on the title only of attachment "a1".

This grouping is clearly shown by the distributions of the metal ratios shown in figure 9 and allows us to reconstruct the sequence of writing the various parts. The whole main folio and the text of attachment "a1" were written at the same time; later, Galileo added attachment "a2" and felt the need of also adding a title to the previous attachment.

In the final part of this report, I would like to point out some of the "methodological" problems that we encountered in the interpretation of the compositional data so far collected about Galileo's inks. They are mainly:

- the dispersion of the detected data;
- the fact that we do not detect some elements, namely sulphur, expected to be present in the ink composition.

Concerning the first point, a rather large dispersion has been often detected in the metal ratios –as measured by PIXE– even when no doubt can be raised on the identity of the ink in different measured spots (e.g. within the same sentence, or line, or even word). This effect can be observed also in figures 7 and 9. Such an effect seems to be larger in *Ms.Gal.72* (undated notes) than in the examined letters or other dated documents. Since the latter ones always belonged to manuscripts where no paper restoration had been performed, while the folios in *Ms.Gal.72* had undergone a restoration prior to our measurement[3], we wonder whether the detected larger dispersion might be related to the washing procedures adopted during paper restoration.

Concerning the problem of missing sulphur, we recall that sulphur is expected in metallo-gallic inks (made by metal sulphates). Sulphur has been indeed found by PIXE measurements in the examined letters, and in *Ms.Gal.26*, while no sulphur is instead detected in any of the so far examined folios of *Ms.Gal.72*. We wonder whether this might have also been produced by restoration.

To better investigate these points, we started a number of tests on metallo-gallic inks of definite known composition *ab initio*: such inks contain different proportions of Fe, Ni, Cu and Zn sulphates and have been prepared according to recipes such as those used at Galileo's times.

The prepared inks have been used to write on a XVII century paper. We wrote at subsequent times: just after preparation, and day by day for the first week, then at longer intervals up to one month. Different conditions at writing have also been simulated, such as preliminary stirring of the ink or not, variable depth of dipping the pen

[3] this restoration had been performed because of a severe deterioration of the paper just due to the acid attack due to the used metallo-gallic inks.

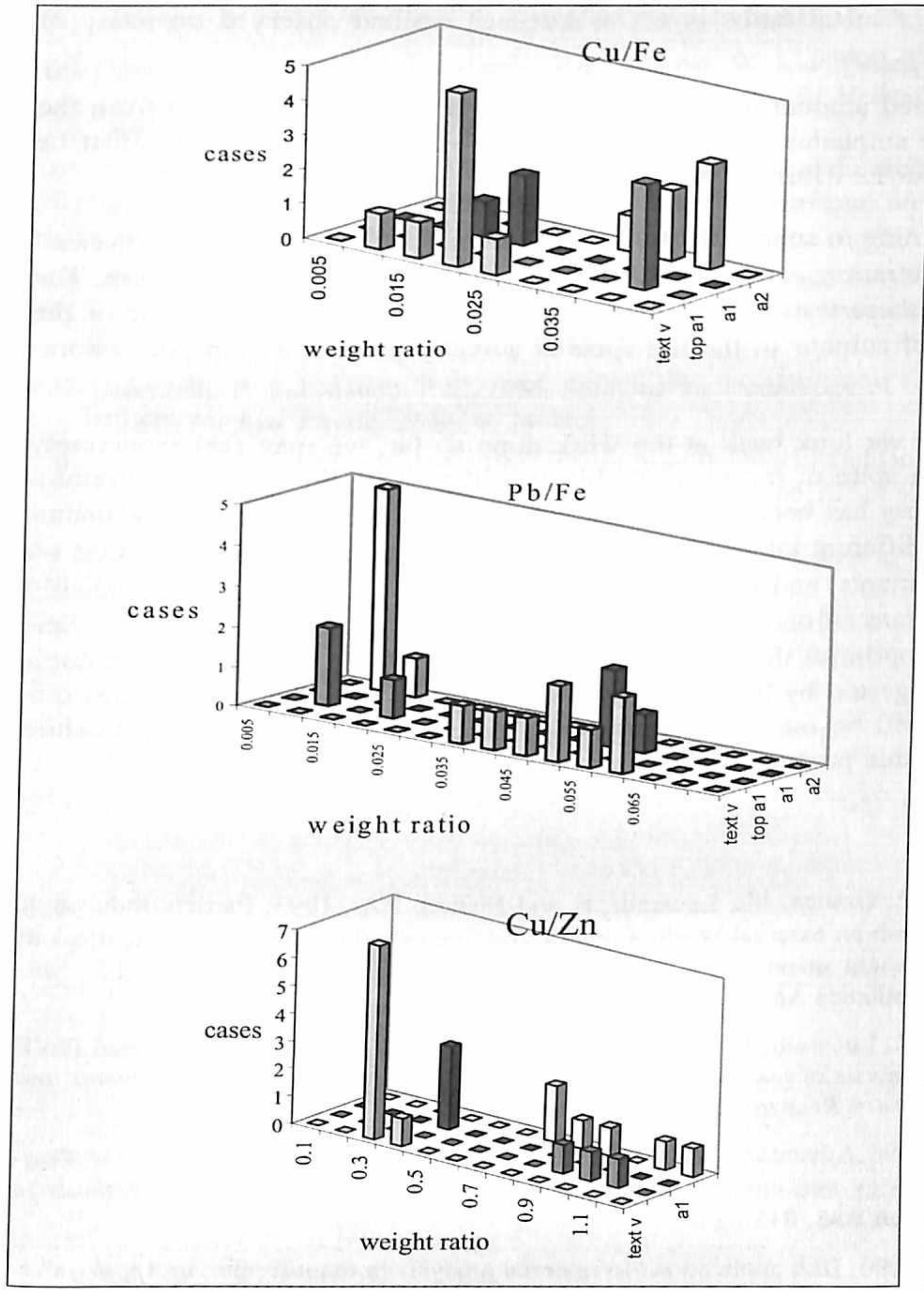

Figure 9. Distributions of the weight ratios measured for Cu/Fe, Pb/Fe and Cu/Zn in the examined spots of ink of the various parts of folio 179v.

in the ink-pot, different pressure of the pen on the paper. Preliminary results on spots of the thus written texts have shown the following:

- the measured composition is quite close to what expected on the basis of the amounts of the various ingredients used. This result increases our confidence on the hypothesis (mentioned above) that matrix effects are not important for a good quantitative measurement of metal ratios in metallo-gallic inks;

• the dispersion of metal ratios is not as large as we had observed on many of Galileo's hand-written notes;

• also the measured amount of sulphur is consistent with what expected from the stoichiometry of the sulphates, although –as expected– some matrix effects must be taken into account for its quantitative evaluation.

We are now planning to submit the folios written with our ink to various processes of ageing and/or restoration, afterwards checking again the apparent composition. The very first results of these tests seem to confirm that at least a drastic decrease of the measured quantity of sulphur in the ink spots is actually produced by paper restoration procedures.

In conclusion, if we look back at the work done so far, we may feel moderately satisfied because, in spite of the many problems still to be solved, even methodologically, some progress has been done and we were often able to discriminate unambiguously between different inks. However, lot of work is certainly still to be done on many undated documents, and more effort is needed to collect a database of reliably dated inks for absolute chronology. A close collaboration with the historians of Science is required to optimise the work in both respects: verifying specific chronological assignments suggested by historical considerations or discriminating between different hypotheses will be our challenging task. We do believe that it is worthwhile spending efforts in this project.

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