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XRF elemental analysis of inks in South American manuscripts from 1779 to 1825

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Abstract

The Regional Archive of Cusco in Peru guards valuable history collections with exceptional regional and international value dating from the sixteenth century to the present. Historical manuscripts are part of the identity of all people; they constitute a tangible cultural heritage that must be studied, valued, and protected. In this sense, the objective of this research was to identify the chemical compositions of inks and paper, with the goals of setting the background of their originality, identifying relationships between them, and glimpsing antecedents that generated degradation due to the compositions of the inks. This study is the first of its kind in Peru and reveals the chemical elements present in the writing ink, the seal, and the paper of five documents from the late eighteenth and early nineteenth centuries. Duplicate in situ nondestructive analyses were carried out using a hand-held X-ray fluorescence spectrometer under ambient conditions in soil mode, configured with three sequential shots, and energies from zero to 40, 40, and 15 keV, respectively. The elements S and Fe were present as components of iron gall inks. Cu and Zn were less abundant; probably, they provided less corrosion and more color intensity to the inks. The minor elements Pb, As, and especially Ag in all manuscripts differentiate them from European inks of the same period. Additionally, the five documents reflect the same elemental compositions but with different concentrations. This could mean that writers used local raw materials and Spanish ink recipes. Finally, the analyses of standard reference material, SRM 1646a and SRM 196b, gave results with acceptable precision.

Keywords: Elemental analysis, Nondestructive characterization, Iron gall ink, Writing ink, Portable XRF, Tupac Amaru II, Principal component analysis, Peruvian manuscript

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Graphical Abstract

Introduction

The Directorate of the Historical Archive is part of the Regional Archive of Cusco (AHC), and it is where manuscripts of historical value are kept. Their documentation dates from the sixteenth century (1545 A.D.) and objects are related to local, national, and South American history. There are reports of valuable documents lost and of illegal trafficking of similar manuscripts from the National Archives [1–3]. Therefore, it is crucial to implement measures that protect them and guarantee their originality, not only to specialists such as paleographers, historians, and experts but also through physicochemical studies of the materials they comprise, using techniques such as chemical elemental analysis. Since it is impossible to remove the documents from the Historical Archive, much less extract parts for research, it is essential to use portable instruments with nondestructive and noninvasive techniques, such as the X-ray fluorescence technique.

Thus, in this paper, five valuable documents housed in the Historical Archive of Cusco and dating back to the eighteenth and nineteenth centuries were studied, not only to disseminate their existence and identify their chemical composition but also to establish scientific grounds for subsequent studies, research or intervention programs. Another reason for the study is to promote institutional methods that protect these written treasures in suitable environmental conditions that guarantee their conservation, implementation of complete restoration programs, access to researchers and society in general.

This study of the chemical compositions of 18th and early nineteenth centuries manuscripts is the first one performed in Peru. For that period, presumably all ink and paper came from Europe and particularly from Spain, and therefore, their compositions should reflect that relationship. On the old continent, black inks had a different origin; the most common were the iron gall inks extensively used in Europe since Middle Ages. These metallic inks follow various formulations, but usually, they were a mixture of tannin/metallic salt/gum/solvent, for which there were diverse formulations. Further, inks containing C or, rarely PbS were reported [4]. Spanish recipes for administrative documents from that time indicate that the main components were oak gall or another source of tannic acid, iron sulfate (vitriol from England) and/or copper sulfate (vitriol from Cyprus), gum Arabic or other material as a preservative, and as a solvent, water or wine [5, 6]. However, this chemical relationship is not very clear since it varies from one place to another.

The elemental compositions of inks, therefore, depend on the contributions of these raw materials; thus, Contreras (2015) used SEM/EDX to analyze inks made with contemporary materials but following old Spanish recipes and found that the galls, the running water of Valencia, the myrtle and Arabic rubber contained Na, Mg, Al, Si, P, S, Cl, K, and Ca [5]. He identified Fe, Mn, Cu, and Zn only in the myrtle and Arabic rubber.

Given the scarcity of galls in Central America and Mexico during the colonial period, native species such as *Caesalpinia coriaria* pods would probably have been used as tannin sources [5, 7]. In Peru, the native species *Caesalpinia tinctoria* or *Caesalpinia spinosa*, commonly known as *tara*, is rich in tannins [8] and has the characteristics needed for the production of inks. Abandoned mines near Cusco still show Fe and Cu minerals, and some of the impurities are Zn, Cd, Pb, Mn, and As. Their higher Fe content [9] could have been a reason for their exploitation in the colonial period, perhaps even for ink

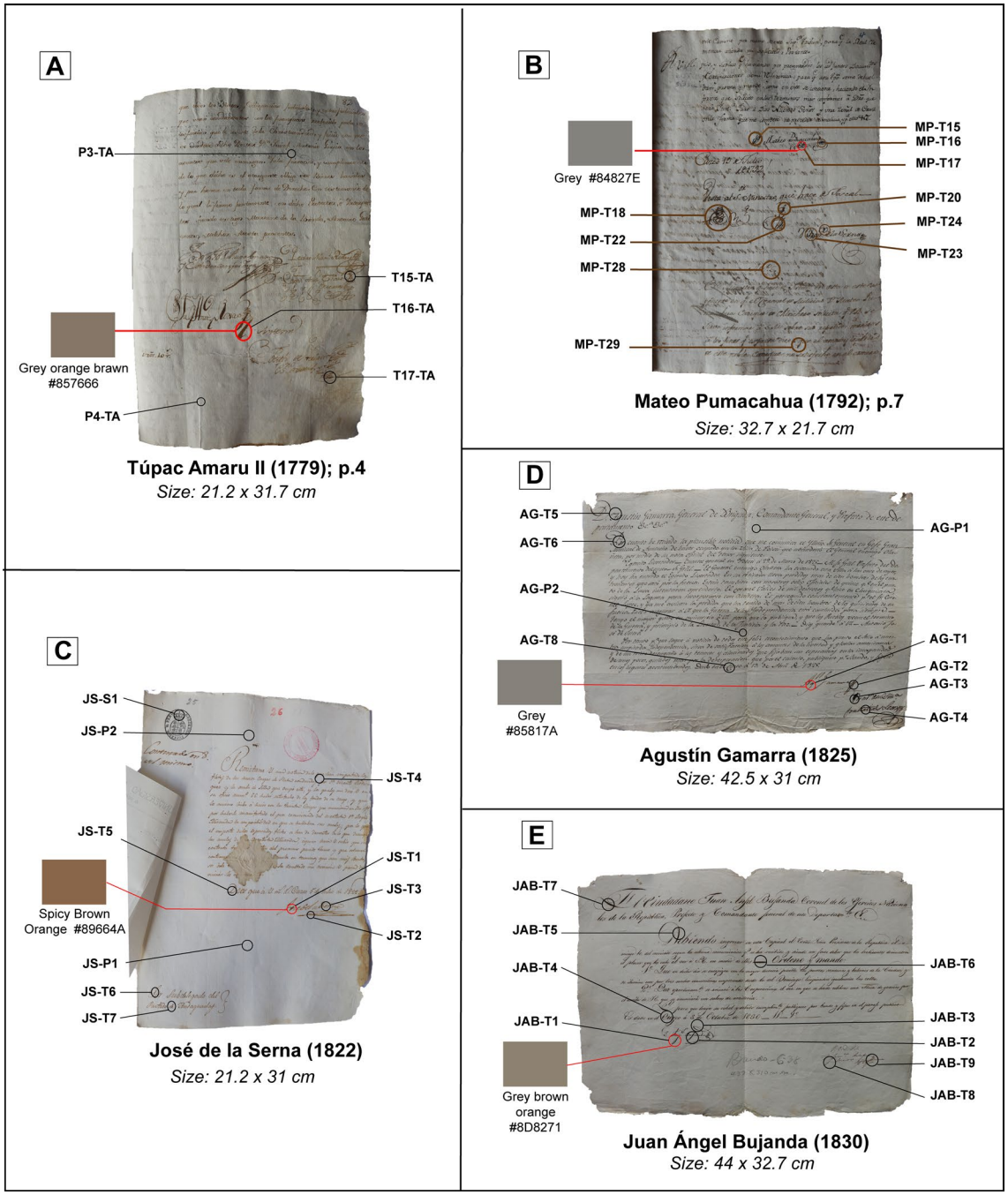

Fig. 1 Studied historical documents (1778–1830). **A** Lawsuit of José Gabriel Tupac Amaru II (1779); **B** Report of Mateo Pumacahua (1792); **C** Order of José de la Serna (1822); **D** Report of Agustín Gamarra (1825). **E** Order of Juan Ángel Bujanda (1830)

production. Therefore, in ancient Cusco, there existed the main raw materials for ink production, and it is worth wondering whether this happened; however, researchers have not found recipes for ink production or records to prove this.

On the other hand, the scriptural support of the documents in the Historical Archive of Cusco is mostly paper, probably of European origin, which at the beginning of the nineteenth century comprised cellulose (cotton, linen, or hemp) adhered with starch, lime (sizing agents) and calcium carbonate, generating a cohesive and resistant material with a basic pH [10].

Among nondestructive analytical methods that do not require sample collection and can be used for the study of iron gall inks from historical documents, the likely choices are X-ray fluorescence, micro X-ray fluorescence analysis (micro-XRF), micro X-ray absorption near edge structure spectroscopy (micro-XANES) [11], Fourier transform infrared spectrometry in the reflection mode (rFTIR) [12], attenuated total reflectance Fourier transform infrared spectroscopy (FT-IR ATR) [13], reflectance UV–Vis spectroscopy [6], Raman spectroscopy [12], and various image analysis techniques [14, 15]. Of these, X-ray fluorescence spectroscopy with portable equipment has been used in various elemental analyses of tangible objects reflecting cultural heritage [12, 16–20], and it produced semiquantitative results guaranteed by repetitive analysis of sampling points or simultaneous analyses of certified reference materials. However, a disadvantage of using these techniques is that there are no papers serving as reference materials with which to certify elemental compositions, making it difficult to analyze inks in historic paper documents.

The end of the eighteenth century to the beginning of the nineteenth century was an era of transition between Viceroyalty and the Republic of Peru. In that period, there was a social movement seeking to put aside the Spanish influence and government. Thus, we can ask ourselves if this current would have influenced emerging sectors in charge of transforming raw materials, convincing them of the need to produce the supplies required for the transformation process, such as inks and papers. In this sense, the objectives of this work were to characterize the elemental composition of inks in five manuscripts from the Cusco Historical Archive (AHC) dated from the eighteenth and nineteenth centuries and identify signs that reveal transformations of matter by the local inhabitants in those years, while recognizing that this is the first study of this type in Peru.

Materials and methods

Researched ancient documents

The documents belong to the Regional Archive of Cusco [21–25]; they have historical value, express important events in Peruvian history, and present signatures of important figures in Peruvian history. They correspond to the eighteenth and nineteenth centuries (Fig. 1). A small description of each follows below:

Doc. 1—Lawsuit of José Gabriel Túpac Amaru II (February 21, 1779).

Table 1 Comparison of experimental and certified values for SRM 1646a and 97b

Element	Experimental value		Certified value		Relative error $\frac{X_{Exp}-X_{Certif}}{X_{Certif}} \times 100$
	SRM 1646a				
	[] ppm	% SD	[] ppm	%SD	
Fe	15,763 ± 69	0.44	20,080 ± 390	1.94	− 21
S	4138 ± 137	3.30	3520 ± 40	1.14	18
Cu	12.3 ± 1.60	13.01	10.01 ± 0.34	3.40	23
Zn	38.7 ± 1.4	3.62	48.9 ± 1.6	3.27	− 21
Mn	173 ± 3	1.73	235 ± 3	1.19	− 26
Pb	9.50 ± 0.90	9.47	11.7 ± 1.2	10.26	− 19
As	7.7 ± 0.80	10.39	6.23 ± 0.21	3.37	24
K	8043 ± 62	0.77	8640 ± 167	1.85	− 7
Ca	3886 ± 39	1.02	5190 ± 200	3.85	− 26
Ti	4041 ± 26	0.64	4560 ± 210	4.61	− 11
	SRM 97b				
Fe	6223 ± 31	0.50	8310 ± 80	0.96	− 25
Mn	39 ± 2	5.13	47 ± 5	10.64	− 17
Sr	83.4 ± 1.5	1.80	84 ± 2	2.38	− 0.7

JGTA sends a lawsuit to the Royal Court of Lima against Don Diego Betancur, who wrongly declared himself a descendant of Don Felipe Túpac Amaru, the last Inca [21].

Doc. 2—Report of Mateo Pumacahua (July 19, 1792).

MP informs the King of Spain of his victories and the latest events against José Gabriel Túpac Amaru's rebellion. The report describes the battles against the rebellion's followers in Calca, Pisac, Ocongate, Puno, and others. There is the signature of Mateo Pumacahua and three members of the Royal Court: Regent, Rezabal and Zernadas, and last is Don Francisco de la Serna' signature [22].

Doc. 3—Order of José de la Serna (July 5, 1822).

JS orders that the cost of transporting freights of silver cargoes be reported, one led by Vicente Rodríguez and the other one from the assent Don Roque Miranda. There is the signature of José de La Serna, and at the bottom, there is a note from the Subdelegate of the Andahuaylas. The manuscript shows large stains of deterioration, perhaps due to spillage of water that erased part of the text and damaged the side edges, which are serious indications of deterioration [23].

Doc. 4—Report of Agustín Gamarra (April 13, 1825).

The General-in-Chief Grand Marshal of Ayacucho AG communicates that he has already occupied the town of Potosí, which the enemy, the general Olañera, left. He assures that the war of independence is concluded forever [24]. Potosi was one of the principal areas of silver mine exploitations.

Doc. 5—Order of Juan Ángel Bujanda (October 8, 1830).

As Prefect of Cusco, he orders that the city's inhabitants upholster with the greatest decency possible the doors, windows, and balconies of the city before the arrival of the President of the Republic, General Agustin Gamarra Messias, as well as light up the city for three consecutive nights. It is signed by the Prefect and his secretary, Don Franco Artajona [25].

The authors seemed to write each of these documents with a specific type of ink, similar to the one used for the signatures; all the manuscripts have brown ink, with different tones and handwriting styles. The support material is paper, and in several of them, there are early signs of deterioration apparently resulting from the effect of humidity, such as yellow spots on the edges. The writer spilled ink in some sectors, and these are areas to watch to avoid deterioration by oxidation.

The XRF analysis of two powdered standard reference materials (SRM) required the use of small containers. SRM 1646a and 97b were placed inside a sample holder and located in the workstation. The holder had a base polypropylene film. The setup simulated a thick layer of SRM over the support material (the film), similar to a pure powdered pigment on paper. Therefore, the X-rays from the portable spectrometer hit the sample directly. The experimental conditions for analyses of the SRMs and the inks were the same. The counts generated by the film were negligible. For each SRM, we calculated the average of ten repetitions per element, and the results are reported in Table 1.

Applied analytical methods

The investigators used in situ DELTA Premiun DP6000 Olympus portable X-ray fluorescence equipment, for elemental analyses of ink and paper. It has a Rh tube, a large surface silicon drift detector, and a power of 4 W under natural environment conditions, a soil mode with three energy ranges: 40, 40, and 15 keV (B1, B2, and B3, respectively), and respective times of 30, 45, and 45 s. The spectrophotometer previously was calibrated with Stainless Steel 316 Calibration Check Reference Coin. The measurements were carried out in the Cusco Historical Archive (AHC) with previous authorization and under staff supervision. The researchers handled the documents with cotton gloves underneath nitrile gloves. Each sheet of the document was placed on a white expanded polystyrene plate (approximately 2.5 cm thick) placed on a wooden table, allowing for results corresponding to analyses of front and back sheets. The 222 selected test points for both ink and paper had no writing on the back sheet The spot size has a 3-mm diameter focused on paper with text.

Before XRF measurements, analysis points were selected on each sheet of the manuscript, including regions where ink existed or did not exist (paper). The evaluated area was carefully cleaned with a soft bristle brush. The equipment was positioned vertically to the analysis point, and two consecutive shots were made; the reported values in ppm correspond to the average. For each element, the spectrometer factory calibration uses two modes: Fundamental Parameters and Compton Normalization Calibration. It allows the instrument to convert the counts to concentration expressed in ppm. In addition, the Compton Normalization reduces effect problems related to surface, texture, and matrix among samples.The instrument has a CCD camera through which the selected analysis area was observed with an approximate diameter of 3 mm.

The X-ray fluorescence spectra were first processed with InnovX software, and simultaneously, with the help

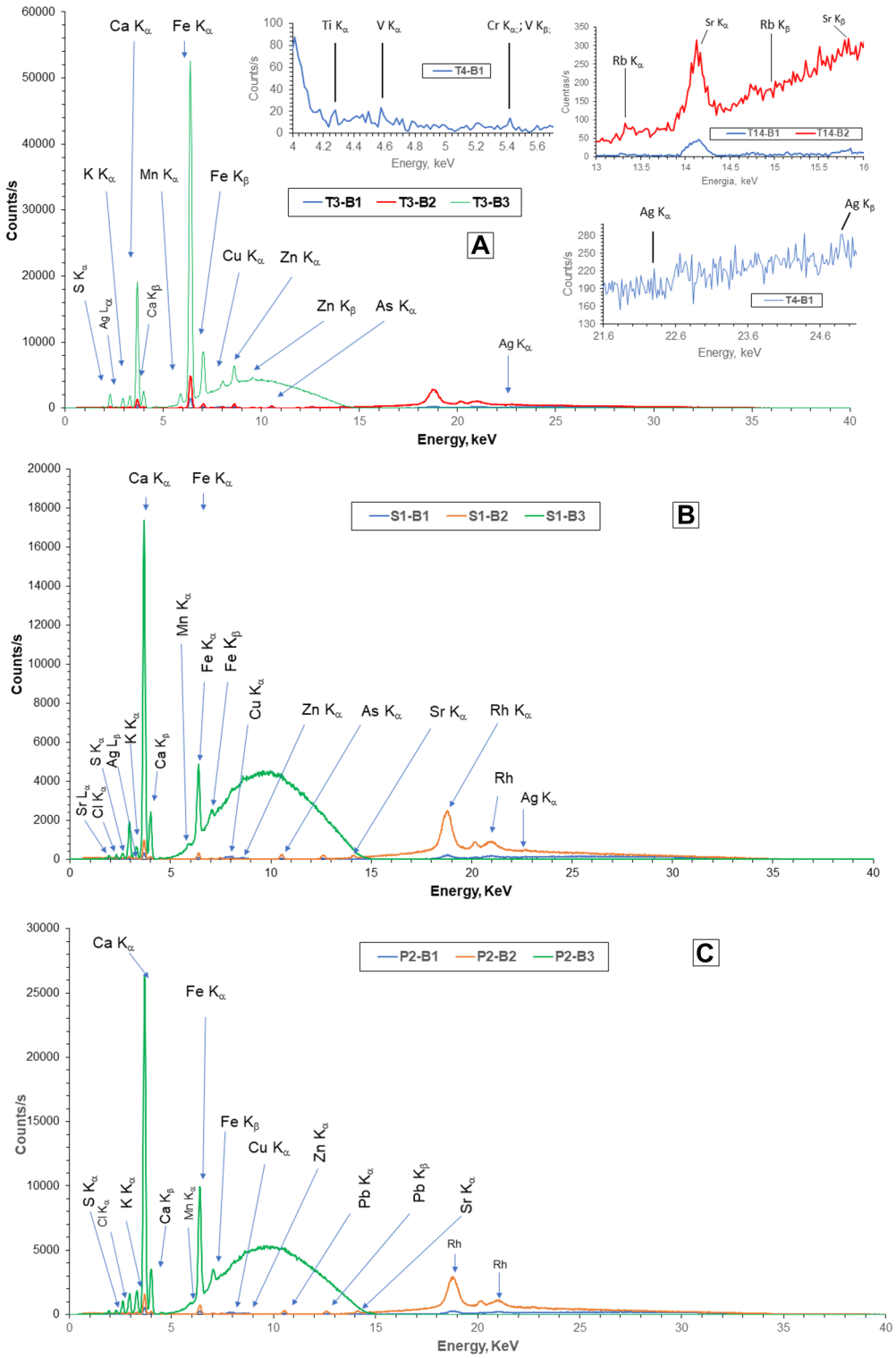

Fig. 2 XRF spectra of Túpac Amaru II's document (1779). Beams B1, B2, and B3. Beams B1, B2, and B3; **A** writing ink; **B** seal or stamp ink; **C** paper

Table 2 Elements present in the papers of the Tupac Amaru II manuscript (eighteenth century)

Element	Elemental composition of the 18th-century paper (ppm)					
	TA-P1	TA-P2	TA-P3	TA-P4	$\bar{x}$	SD
S	7199 ± 194	7940 ± 215	9040 ± 243	6610 ± 198	7697	907
Cl	1801 ± 52	7587 ± 100	2817 ± 70	5229 ± 83	4359	2242
K	1385 ± 33	5152 ± 58	2409 ± 47	5230 ± 58	3544	1687
Ca	40,505 ± 185	50,352 ± 233	56,094 ± 274	50,794 ± 231	49,436	5630
Ti	65 ± 3	91 ± 4	103 ± 4	82 ± 4	85	14
V	23.8 ± 0.9	27.5 ± 1	33.9 ± 1.2	25.1 ± 1	28	4
Cr	101 ± 2	114 ± 3	128 ± 3	112 ± 3	114	10
Mn	264 ± 4	307 ± 4	343 ± 4	284 ± 4	300	29
Fe	990 ± 17	1672 ± 24	1179 ± 22	795 ± 15	1159	326
Cu	8 ± 2	20 ± 3	70 ± 4	51 ± 3	37	25
Zn	13.3 ± 1.5	28.8 ± 2	29 ± 2	22.7 ± 1.7	23	6
As	22 ± 2	30 ± 3	22 ± 2	19.8 ± 1.9	23	4
Rb	5.1 ± 0.6	4.2 ± 0.7	6.4 ± 0.8	4.9 ± 0.6	5	1
Sr	19.4 ± 1.1	22.8 ± 1.3	25.1 ± 1.5	24.2 ± 1.2	23	2
Pb	107 ± 3	148 ± 3	89 ± 3	72 ± 2	104	28
Ag	27 ± 4	17 ± 4	17 ± 5	24 ± 4	21	4

TA José Gabriel Túpac Amaru II, $\bar{x}$ Average, *SD* Standard deviation

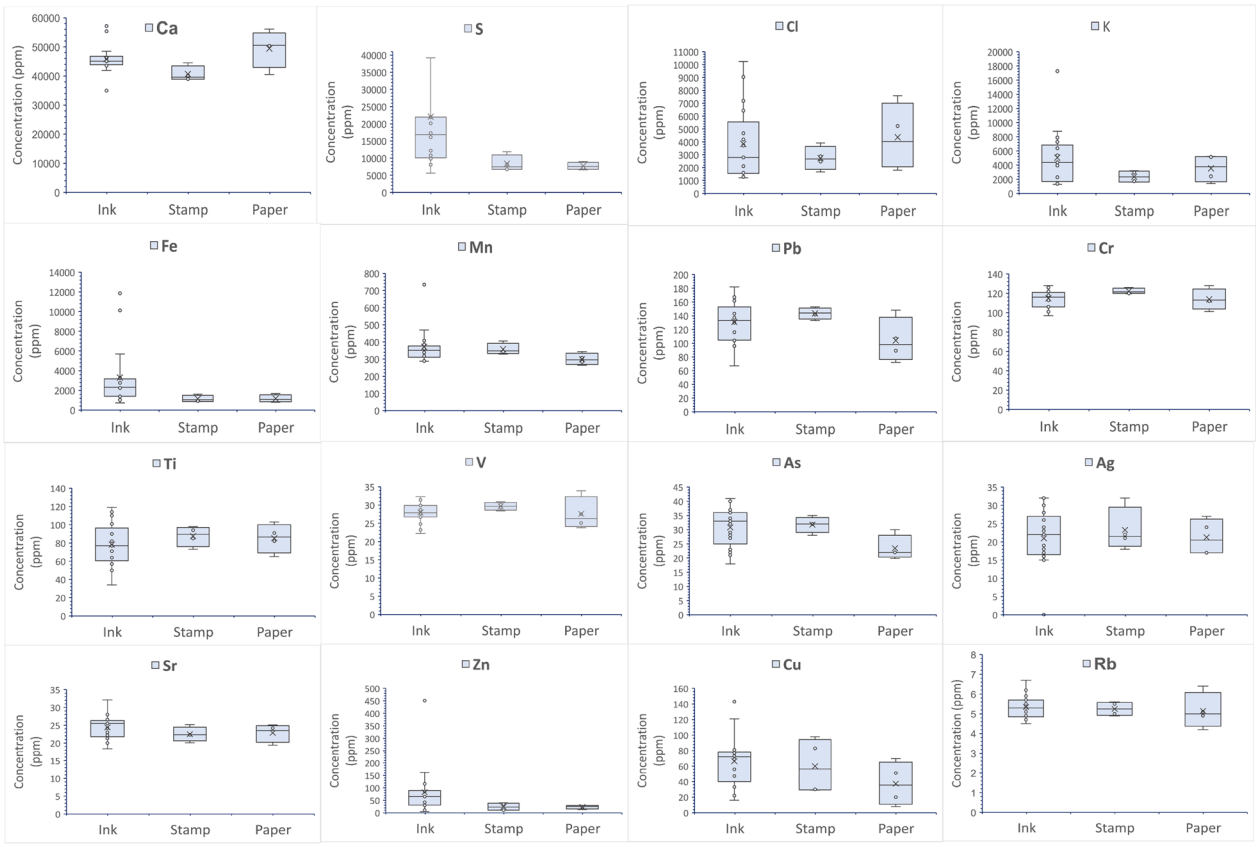

Fig. 3 Variation of elemental composition of materials in the J.G. Túpac Amaru II document (1779)

of an X-ray energy table [26], the presence of chemical elements was confirmed by direct observation of the spectrum and the energy peaks for each item, which will be reported below. Later, the InnovX data file was processed, considering the confirmed elements in the spectra and their average elemental compositions (ppm). All concentrations (ppm) reported are superior to their respective LOD [27]

Principal component analysis (PCA) used this chemical composition. This chemical composition was used for the main component analysis. Principal component analysis of Mateo Pumacahua inks (Doc. 2) was performed using Pirouette v4.5. Initially, we used 27 samples (writing ink analysis points), 12 variables (confirmed minority elements Mn, Cr, Zn, Ti, Cu, V, Ag, Sr, Pb, As, Rb and Mo), preprocessing of the "variance scale" to avoid conflicts of the unit scale, and six factors, representing the highest possible variance (99%). Subsequently, outliers T7, T11, T28, and T30 were excluded and ten new analysis points (signatures) in the manuscript (T15 to T24) were included, and a new PCA was performed under the same conditions used previously.

The raw data of this manuscript will be accessible in the repository of Mendeley Data [28].

Results and discussion

The spectra for the inks showed Ca, S, Cl, K, Fe, Mn, and Pb in higher counts and Cr, Ti, V, As, Sr, Zn, Cu, Ag, and Rb in lower counts. Comprehensive analysis of the spectra showed the energies of K_α, K_β, L_α, or L_β peaks of the identified elements (Fig. 2).

Elemental analysis of the paper

The manuscript of J.G. Túpac Amaru II (1779) consists of 4 sheets. Four inkless paper spots were analyzed (P1, P2, P3, and P4) with two repetitions in areas that appeared to be in good condition at first glance. Sixteen chemical elements were found (Table 2), such as Ca and K, which can be explained because, historically, compounds of these elements have been used as a support to fill the pores and lighten the color of paper [10]. Points P1 and P2 are on the first sheet, and P3 and P4 are on the last sheet where the signatures appear. The presence of S, Fe, Mn, Pb, and the other minor elements could be due to migration of the ink components in the paper or the contribution of vegetable raw materials and water used during its production. The presence of chlorine could also be due to the type of water used in preparation of the paper [5].

The elemental compositions of the papers used for the next four manuscripts evaluated were similar, and we will not present a detailed discussion of them.

Table 3 Elements present in the manuscript of Mateo Pumacahua (eighteenth century)

Element	Average concentration (ppm)			Olympus Delta Premium DP6000 LOD (ppm)[d]
	Ink[a]	Stamp[b]	Paper[c]	
Ca	21,069 ± 5448	23,047 ± 2777	26,341 ± 3570	10–35
S	30,966 ± 17,124	13,332 ± 2555	7316 ± 3632	50–150
Fe	6324 ± 3245	2692 ± 456	1407 ± 348	5–20
Cl	3002 ± 780	3148 ± 453	4896 ± 1476	–
K	2894 ± 1131	1600 ± 501	1336 ± 270	20–50
Mn	251 ± 12	258 ± 13	254 ± 7	3–7
Cr	91 ± 7	100 ± 6	99 ± 3	2–9
Zn	79 ± 32	110 ± 6	102 ± 12	1–3
Ti	43 ± 14	71 ± 7	76 ± 40	5–10
Cu	29 ± 22	43 ± 11	17 ± 11	2–6
V	23 ± 3	30 ± 3	28 ± 3	4–10
Ag	20 ± 3	23 ± 5	19 ± 3	5–12
Sr	13 ± 4	16 ± 3	15 ± 4	1–2
Pb	7.6 ± 3	53 ± 13	6.8 ± 2.5	1–4
As	4.3 ± 1.1	20 ± 5	4.3 ± 1.4	1–3
Rb	3.9 ± 0.8	4 ± 1	3.8 ± 0.4	1–2
Mo	4.2 ± 0.6	3 ± 2	3.6 ± 0.4	1–2

[a] n = 40

[b] n = 6

[c] n = 5; n = number of analyzed points; $\bar{x}$ = Average; SD = Standard Deviation

[d] [27]

Elemental analysis of inks

Manuscript of José Gabriel Túpac Amaru II (1779)

As indicated before, the manuscript has four sheets with handwritten texts, a letterhead stamp on the top edge of each sheet, and five signatures. The major elements found in the writing ink (Fig. 3) were Ca, S, Cl, K, Fe, Mn, Pb, Cr, Ti, and the minority were V, As, Ag, Sr, Zn, Cu, Ag, and Rb. That is, the elemental components are the same as those in the paper, but in different concentrations. The more significant components are Fe and S, which are components of iron gall ink.

Spanish iron gall inks originating from the XVIII and XIX centuries present the same major elements and different contents of minority and trace elements. The writing and stamping inks of Cusco manuscripts confirm with this statement. The presence of Cu, Zn, As, Ag, and Rb separates them from those reported in contemporary European documents.

The presence of Cu and Zn could be intentional or could come from raw materials [5]. By the nineteenth century, it was already known that $CuSO_4$ caused less

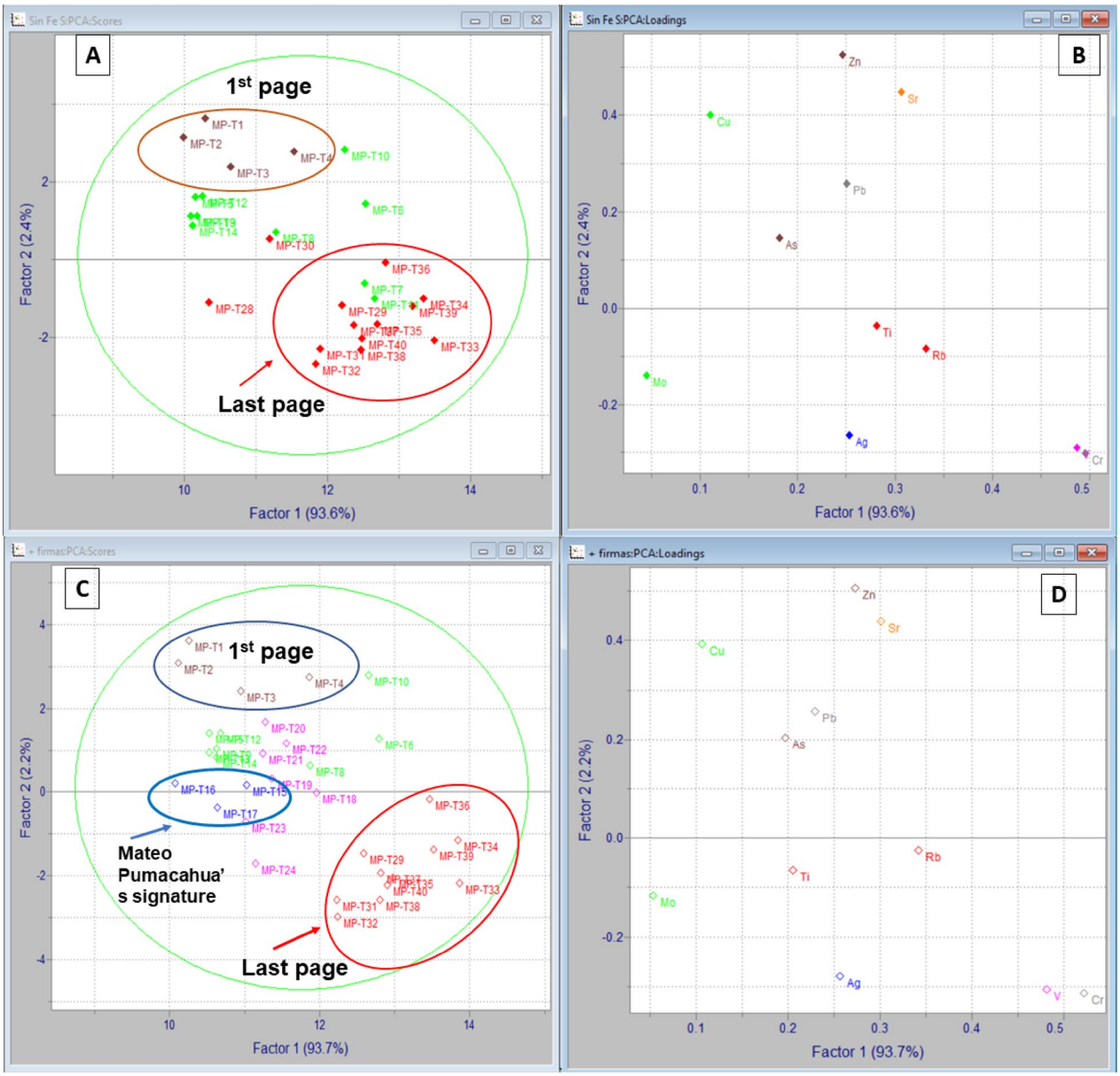

Fig. 4 Manuscript of Mateo Pumacahua (1792): Classification of writing inks using PCA. **A** brown- annotation on the first sheet; green—the body of the text; red—annotation on the last sheet; **B** Loadings corresponding to "A". **C** Blue—the signature of Mateo Pumacahua; lilac = other signatures; **D** Loadings corresponding to "C"

deterioration of paper and that $ZnSO_4$ produced a darker ink. However, both Cu and Zn are present in the minerals used to obtain $FeSO_4$ and in vegetable sources of tannins (galls or an Andean species such as *tara*) [8].

The stamp and writing ink have similar chemical elements (Fig. 3). Therefore, the median values are different; for example, the median of the stamp ink is slightly higher only in the minor elements Pb, Cr, Ti, and V. This implies that different recipes were used according to use of each kind of ink for writing or stamping. Considering that Ca was used as $CaCO_3$ to correct the acidity of the wine [5] and the Ca average concentration in stamp ink is lower than that found on paper ($CaCO_3$ can also be used as filler to increase paper opacity and brightness), it is possible to suppose that water was used instead of wine for production of this ink as well as for writing.

This use of water probably caused the rapid decomposition of ink due to the action of microorganisms,

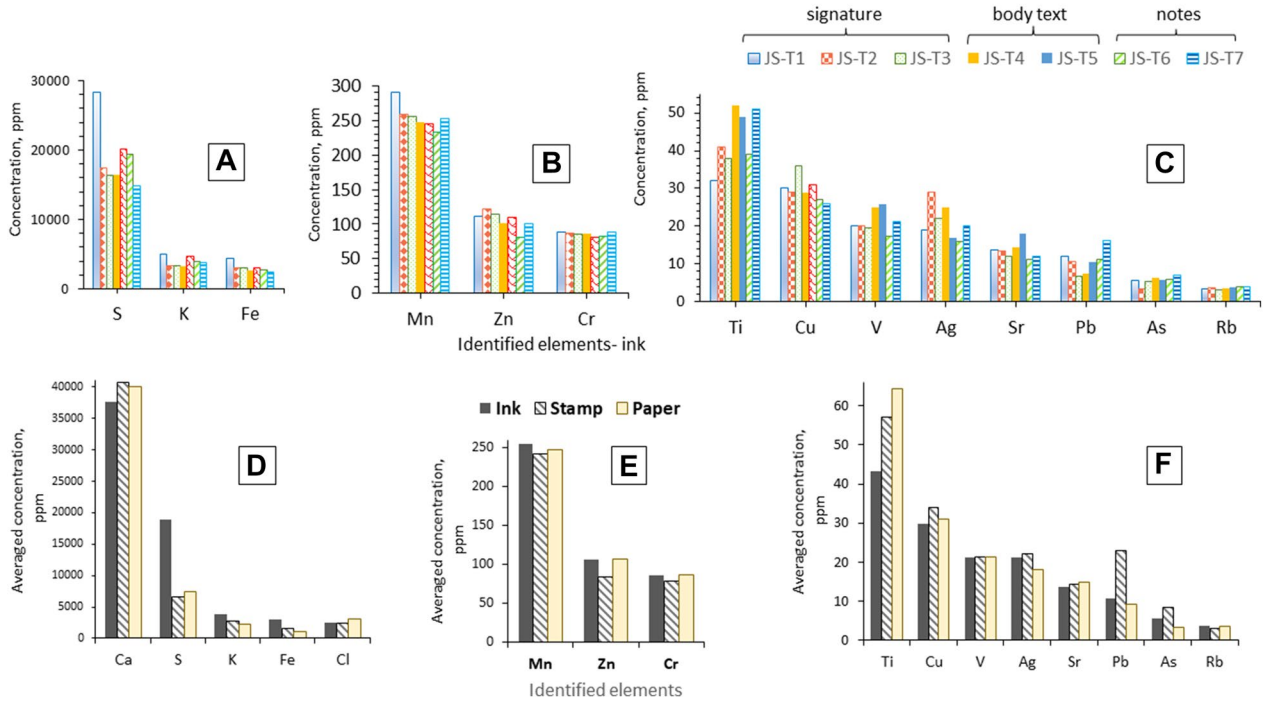

Fig. 5 The average elemental composition of materials in Jose de la Serna's document (1822). *Writing ink composition*: **A** elements with major concentrations; **B** elements with intermediate concentrations; **C** elements with lower concentrations. *Comparison between ink, stamp, and paper*: **D** elements with major concentrations; **E** elements with intermediate concentrations; **F** elements with lower concentrations

and, therefore, As compounds would have been used to extend the useful lifetime. Lead would have already come from inkwells or the containers used during the purification of Fe compounds.

Mateo Pumacahua (1792)

This is a seven-sheet manuscript; each front side contains a stamp in the upper left corner, and, at the end, there are five signatures and annotations on the first and last sheets. Some sheets show ink stains and signs of deterioration. The stamps, handwritten text, signatures, and paper were analyzed. Discussion of impaired areas is not presented in this article.

The manuscript length gives rise to great heterogeneity in the composition of the ink due to recharge during the writing process [29]. At the ink analysis points (T1 to T40), the following elements were found in order from highest to lowest concentrations (ppm): Ca, S, Fe, Cl, K, Mn, Cr, Zn, Ti, Cu, V, Ag, Sr, Pb, As, Rb and Mo; this was true of the stamp ink (S1 to S6), although with different concentrations (Table 3). Here, also, the stamp ink had a higher As content. The averages presented high deviations, reflecting little homogeneity between evaluated points, which is consistent with the fact that they are different sheets and that, to write a relatively long document, it is necessary to "reload" the pen several times and perhaps "refresh" the ink. This dispersion of values is repeated for the stamp ink and for the paper.

For principal component analysis (PCA), Ca, K, and Cl were excluded due to their relationship with the paper, and S and Fe were excluded because they were the major components. The PCA results corresponded to 99% of the variance; PCA used 27 samples, 12 variables, variance scale preprocessing, and 6 factors. PCA allowed us to differentiate the inks into three classes, according to their location in the manuscript (Fig. 4A): 1) the annotation on the upper left on the first sheet (T1 to T6); 2) the body of the text (T7 to T14), and 3) the annotation at the end of the last sheet (T28 onwards). Although some points exhibiting contradictory behavior are observed (T7, T11, T28, and T30), it is clear that the three segments (Fig. 4C) were written with inks of different chemical compositions, especially for copper, zinc, and lead (Fig. 4B and C).

Mateo Pumacahua's signatures (T15, T16, and T17), the three unnamed rubrics (T18, T19, T20, and T22), and the second illegible signature (T23 and T24) in the

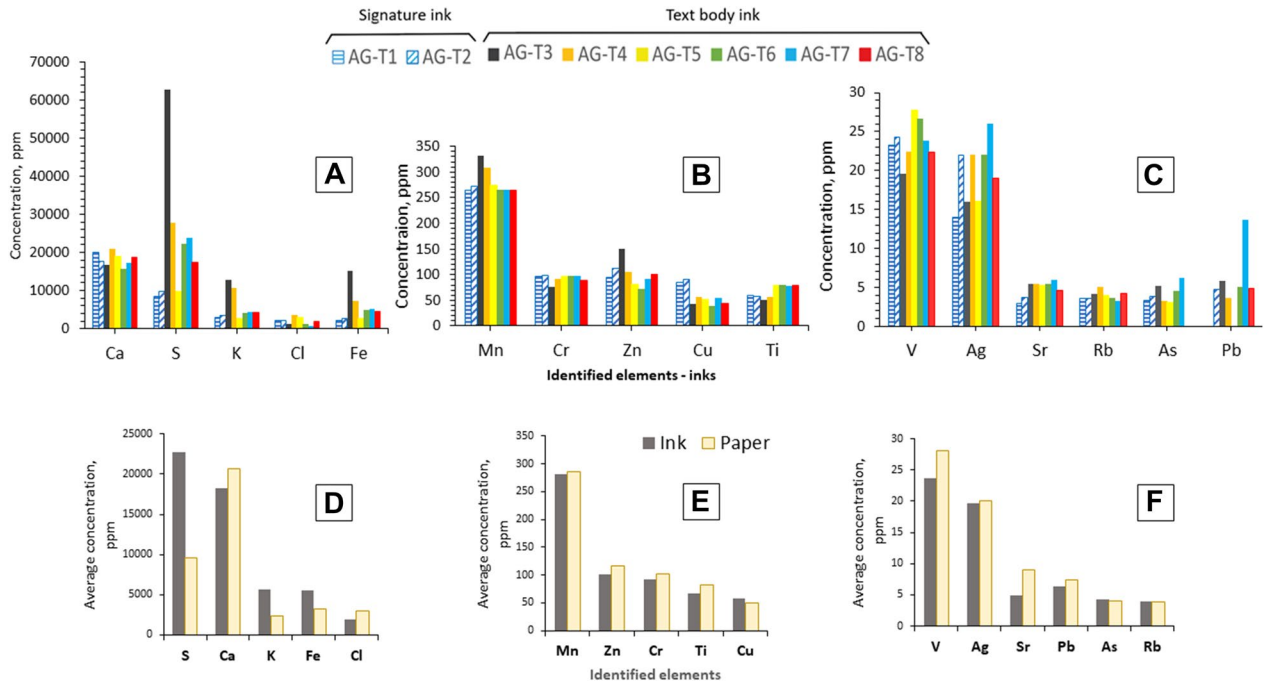

Fig. 6 Elemental compositions of ink and paper in the Agustín Gamarra manuscript (1825). **A** major elements; **B** intermediate concentrations; **C** minor elements; **D**–**F** Identified elements in paper and ink

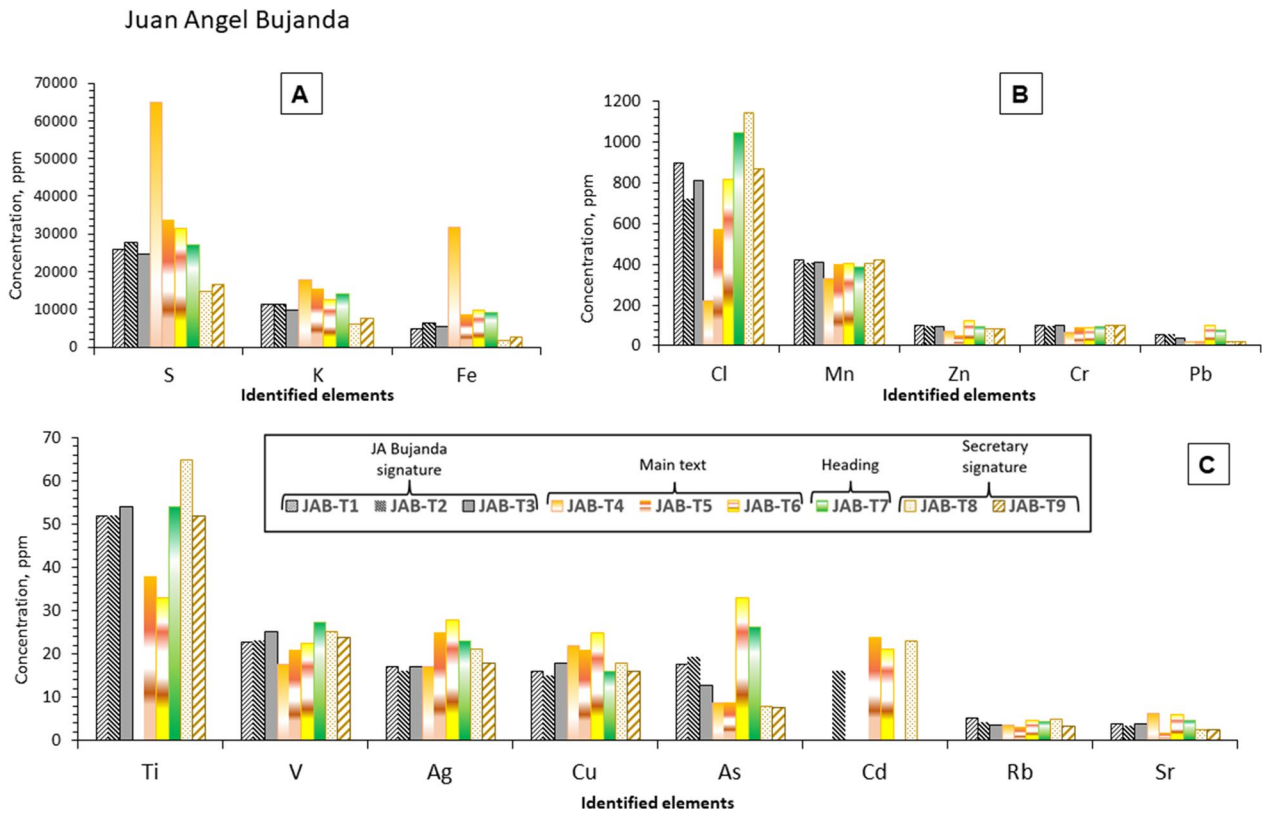

Fig. 7 Elemental compositions (ppm) of the inks. Manuscript of Juan Ángel Bujanda (1825). **A** elements with major concentrations; **B** elements with intermediate concentrations; **C** elements with lower concentrations

previous model (Fig. 4C) have their elemental compositions grouped with the inks used for the body of the manuscript text. This suggests that signatures and text were written with the same ink; annotations were made with a second ink or at least at another time; and Mateo Pumacahua (T15, T16, and T17) would have used the same ink used in the body of the text.

Given the historical importance of this manuscript demonstrating the anti-independence actions of Pumacahua, one cannot help but wonder why someone who had fought in favor of the Spanish king would not have a range of materials at their disposal.

José de la Serna (1822)

This is a one-sheet manuscript with 10 points analyzed; it contains a signature (JS-T1, JS-T2, and JS-T3), a stamp of the Superior Government of Peru (JS-S1) in the upper left corner, and notes on the lower left side (JS-T6 and JS-T7). Two additional points were evaluated in the central text paragraph (JS-T4 and JS-T5). The spectral analysis confirms the presence of Ca, S, K, Cl, Fe, Mn, Cr, Zn, Cu, Ti, V, Ag, Sr, Rb, As, and Pb (Fig. 5). The ink in the main text and in José de la Serna's signature have similar elemental concentrations (ppm). The Fe and S contents at point JS-T1 generated a high relative standard deviation (RSD) 21% and 22%, respectively, probably because it is a dot of ink "spilled" on the signature. The body text and the signature element concentrations indicate the use of the same ink; that is, Jose de la Serna would have written both. Further studies of paleography, calligraphy and physicochemical compositions of other texts containing the famous man's signature could help confirm this hypothesis.

This highlights that the stamp and writing ink compositions differ in S, Fe, Zn, Ti, Cu, Pb, and As contents. Lead (23 ppm) and arsenic (8 ppm) were present in the stamp, as in other stamp inks evaluated in this research. However, these elements are present in concentrations too low to categorically affirm this variability using only in situ portable XRF.

During the vice-royal period in Peru, the exploitation of silver was one of the most important mining activities, and ores contained lead and other minor elements. Lead was also exploited and used to make various containers, including tanks in which inks were stored [9]. These facts can explain the source of this metal in Peruvian inks.

The inks of the JS document and previous documents contain Ag; consequently, we propose the following hypotheses for its presence: 1) The use of silver in inkwells and ink storage containers induced the migration of this metal into the ink; 2) Lead inkwells were made from local raw materials, which underwent incomplete

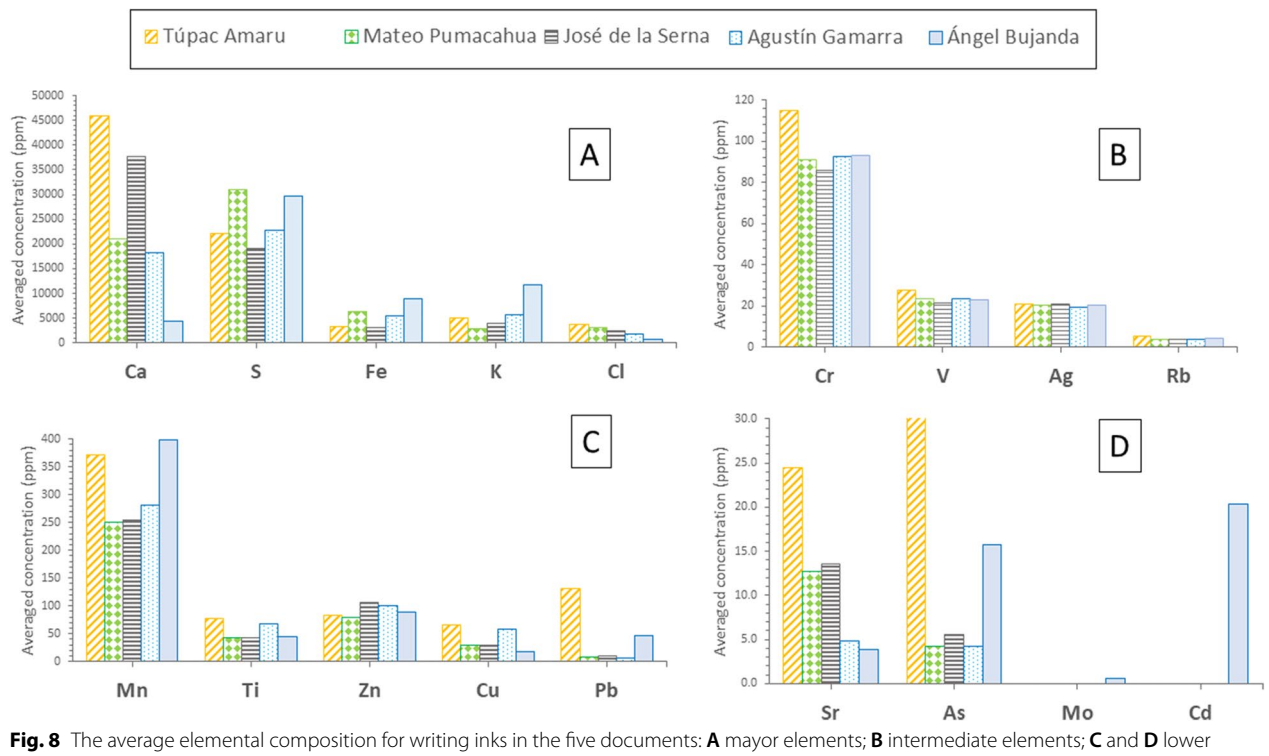

Fig. 8 The average elemental composition for writing inks in the five documents: **A** mayor elements; **B** intermediate elements; **C** and **D** lower elements

artisanal smelting, so they still contained low concentrations of silver and other metals that could migrate into the ink; 3) There were storage conditions that favored metal migration into the ink, such as an acidic pH, perhaps related to the use of urine. The verification of these hypotheses must be undertaken in other studies of ancient inks.

Manuscript of Agustín Gamarra (1825)

This is a one-sheet manuscript containing three signatures. The first is from Agustín Gamarra (AG-T1 and AG-T2), the Constitutional President of Peru (1829 to 1833), and the second is probably an annotation from the secretary (AG-T3) and his heading (AG-T4). Ten ink spots (AG-T1 to AG-T8) and two paper spots from an area in good condition and without ink (AG-P1 and AG-P2) were analyzed. The major elements (Fig. 6A) found in the inks were Ca, S, K, Cl, and Fe; those with intermediate concentrations (Fig. 6B) were Mn, Cr, Zn, Cu and Ti, and the minor elements were V, Ag, Sr, Rb, As and Pb (Fig. 6C). The paper contains similar elements, but in different concentrations (Fig. 6D, E and F). The ink used in AG-T3 was clearly different from the ink of the text; perhaps it was added after the writing of the manuscript, and this highlights its higher proportions of S, Fe, and Zn. Agustín Gamarra's signature, that of the notary, and the rest of the text coincide in elementary composition, which allows us to suppose that it was written in its entirety with the same dyeing material.

Juan Ángel Bujanda Unsuluarte (1830)

This one-sheet manuscript in band format contains the heading (JAB-T7), the main text (T4, T5, T6), and two signatures at the bottom, one of the prefect Juan Ángel Bujanda Unsuluarte (JAB-T1, JAB-T2) in the new Republic of Peru and (JAB -T3) and the second from his secretary Don Franco Artajona (JAB-T8 and JAB-T9). Additionally, two more inkless papers (JAB-P1 and JAB-P2) were analyzed.

The elements found in the inks were S, K, Fe, Cl, Mn, Zn, Cr, Pb, Ti, V, Ag, Cu, As, Cd, Rb, and Sr (Fig. 7). Their concentrations revealed the use of at least three different inks. The first corresponds to the JAB signature, for which contents differ from those in the secretary's signature and in the body of the text, especially in its contents of major elements S and Fe and minor elements Pb and As. The second is the ink of the secretary's signature that is different from that used in the text. The third corresponds to the body text and heading. These findings suggest that the ordinance was written by a third person or with a third material.

A broad comparison of the inks of the five documents allows us to affirm that they all have similar elemental compositions and differ in the concentration that made them unique. Furthermore, the Bujanda manuscript is the only one that contains Cd.

Elemental analyses of standard reference material 1646a and 97b

The precision obtained is acceptable. In the case of SRM 1646a, the elements Fe, S, Zn, and Mn gave %SD = 0.44%, 3.30%, 3.62%, and 1.73%, respectively, while Pb and Cu gave %SD = 9.47% and 13.01%, respectively. The precision for the analysis of SRM 97b was of the same order.

The %SD values showed data clustered around the measured value and thus confirmed repeatability. When comparing the experimental values of both SRMs with their respective certified values, the relative error was approximately 20%. This is probably because the certified SRMs correspond to the analysis of a 500 mg sample, and in our case, it was an in situ microanalysis.

Features and differences between the ink composition of the five documents

These manuscripts cover around 52 years, and even though each document contains different inks, it is possible to observe the changes through the years. It must be considered that the values gave greater variation when they represented a group of data with different ink types, while a small diversity means that similar or the same inks were used in one document. The Tupac Amaru II manuscript (1779) inks differ from the others as there is a bigger presence of Ca, Cl, Mn, Pb, Cr, Ti, V, As, Sr, and Rb than in other inks (Fig. 8A). Also, the simultaneous presence of Pb (131 ± 9 pm; Fig. 8C) and As (31 ± 7 ppm; Fig. 8D) could be related to contaminated waters or to a mineral source.

Mateo Pumacahua wrote the manuscript (1792) when he fought against Tupac Amaru II, and he probably traded raw material brought from Spain with Spanish suppliers. Pumacahua's inks show more S (30,966 ± 17,124 ppm) and Fe (6324 ± 3245 ppm), compared with Tupac Amaru II (22,059 ± 18,697 ppm S and 3303 ± 3039 ppm Fe) and other inks, Pumacahua's inks possibly used purer $FeSO_4$ than Tupac Amaru II's ones. Jose de la Serna's ink (1822) stands out in Zn content (106 ± 12 ppm). Agustin Gamarra (1825) and Ángel Bujanda's (1830) manuscripts correspond to the first years after the independence of Peru and other Latin American countries, but their inks are not similar, for example, Lead is less present in Agustín Gamarra's ink (6 ± 3 ppm Pb versus 46 ± 28 ppm As). Moreover, it is interesting to observe that the average contents for Ag, V, and Cr in all inks are analogous

(Fig. 8B); that is to say, the presence of these elements could be the same.

Conclusion

The elemental compositions of the evaluated manuscripts are the first ones identified in Peru, and this constitutes the basis for later studies of historical documents in the Regional Archive of Cusco. This set of values unequivocally characterizes each of them, guarantees their originality, and highlights their value as items with cultural heritage. The compositional fingerprint guarantees authenticity in cases of loans, before, during, and after their return, and in cases of loss, and subsequent conservation/restoration interventions, and provides physicochemical support of Peru's statements of history.

The ink's elemental composition present in the five documents, which date from 1779 to 1830, reveal a greater content of (ppm) Ca, S, Fe, Cl, and K. Both S and Fe, that are the chemical fingerprint of the use of iron gall inks. Mn, Cr, Zn, Ti, Cu, V, Ag, Sr, Pb, As, Rb, Mo, and Cd are in lower concentrations. This combination (ppm) differ from European inks, specifically in Pb, As, and Ag. The values below are averages of the diversity of inks identified in each manuscript, so they should be considered in this context. The largest standard deviation implies the use of several inks in the same document. Ag is found almost homogeneously in the five inks. Its presence is slightly higher in the manuscripts of José de la Serna-1822 (21 ± 4 ppm Ag) and Tupac Amaru II-1779 (20.9 ± 7.7 ppm Ag) compared with those of Agustín Gamarra-1825 (19.6 ± 3.8 ppm Ag), Mateo Pumacahua-1792 (20 ± 3 ppm Ag) and Juan Ángel Bujanda-1830 (20 ± 4 ppm Ag). The presence of Ag marks its difference with contemporary European inks, as there are no known reports in this regard. It is also worth highlighting the parallel presence of Pb and As in the ink of the Tupac Amaru-1779 document (131 ± 29 ppm Pb and 31 ± 7 ppm As), as in the document by Juan Ángel Bujanda-1830 (46 ± 28 ppm Pb and 16 ± 9 ppm As). Undoubtedly, the documents of Agustín Gamarra, José de la Serna, and Mateo Pumacahua report lower Pb and As contents due to the use of other raw materials, feasibly with fewer pollutants.

The presence of diverse elements, such as Ag, Cu, Zn, and As generates questions that open up new research routes. For example, the Cusco inks clearly followed the Spanish recipes; consequently, why do they contain Ag when the European ones did not? Could this be attributed to the presence of silver in containers used for storage of the ink or in silver inkwells? If so, what physicochemical conditions would lead to such migration? Would lead inkwells have been made from an incipient transforming industry in Peru using less valuable metals? Were Cu, Zn, and As added intentionally to obtain an ink with specific characteristics that was less corrosive, darker, and more durable?

These questions and the fact that in the Inca epoch, they knew of the dyeing power of plants, animals, lichens, and other Andean raw materials, and considering the existence of the Cusco School of Art during the Viceroyalty allow us to suppose that, in the age of the evaluated manuscripts, the conditions and materials for ink production existed. Therefore, the inhabitants who knew this process could write their essays by using local raw materials and creating the ink variety that we found.

Abbreviations

SRM: Standard reference material; $\bar{x}$: Average; SD: Standard deviation; RSD: Relative standard deviation.

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Authors' contributions

CLO was responsible for conceptualization, methodology, writing-original draft preparation, and data analyses. MAZJ was responsible for XRF analyses, data curation, writing-reviewing, and visualization. FLRA was responsible for the investigation, data collection, and XRF analyses of inks. YJCH was responsible for XRF analyses of inks and papers. JFGB was responsible for supervision, writing editing, and visualization. Jorge Olivera Olivera was responsible for historical investigation and writing-reviewing. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets of elemental composition generated and analyzed during this study are available in Mendeley Data as "Elemental analysis XRF of inks (1778–1825)". Reserved https://doi.org/10.17632/228pwkw55h.1

Declarations

Competing interests

The authors declare that they have no competing interests.

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