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Review on the Analysis of Questioned Documents

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Graphical abstract

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Highlights

- A comprehensive and critical review on the analysis of questioned documents is described.
- Analysis of pen inks through a wide range of analytical techniques is discussed.
- Most relevant articles on other samples related to questioned documents are reviewed.
- Trends in the analysis of questioned documents are concluded.

Abbreviations

AAS: atomic absorption spectroscopy

ACN: acetonitrile

AES: atomic emission spectrometry

AlB: alkyl benzene

AlR: alkyd resin

ATR: attenuated total reflectance

BA: benzyl alcohol

BGE: background electrolyte

BTA: benzotryazole

CA: cluster analysis

CE: capillary electrophoresis

CZE: capillary zone electrophoresis

C.I.: colour index

DAD: diode array detector

DART: direct analysis in real time

DCM: dichloromethane

DEG: diethylene glycol

DESI: desorption electrospray ionization

DGPE: diethylene glycol phenyl ether

DHB: 2,5-dihydroxybenzoic acid

DMF: dimetilformamide

DP: discrimination power

DP: dyoctil phthalate

DPG: dipropylene glycol

DTG: di-o-tolylguanidine

EASI: easy ambient sonic-spray ionization

EASY: easy ambient

ED: energy dispersive

EDS: energy dispersive X-ray spectrometry

EG: ethylene glycol

ER: epoxy resin

ESI: electrospray ionization

EtOH: ethanol

FAB: fast atom bombardment

FID: flame ionization detector

FLE: filtered light examination

Fluor: fluorimetry

FTIR: Fourier transformation infrared

G: glycerine

GC: gas chromatography

HSI: hyperspectral imaging

HPLC: high performance liquid chromatography

HPTLC: high performance thin layer chromatography

ICP: inductively coupled plasma

IMS: imaging mass spectrometry

INAA: instrumental neutron activation analysis

IR: infrared

IRL: infrared luminescence

IRR: infrared reflectance

LA: laser ablation

LD: laser desorption

LDA: linear discriminant analysis

LDI: laser desorption ionization

LED: light emitting diode

LIBS: laser induced breakdown spectroscopy

MALDI: matrix assisted laser desorption ionization

MECC: micellar electrokinetic chromatography

MeOH: methanol

MK-FTIR: microespectrometry in infrared

MMA: methylmethacrylate

MS: mass spectrometry

MSTFA: N-methyl-N-trifluoroacetamide

NACE: non-aqueous capillary electrophoresis

NIR: near infrared

NMP: N-methyl-2-pyrrolidone

OA: oleic acid

PAL: palmitic acid

PCA: principal component analysis

PCs: principal components

PDAD: photo diode array detector

PE: phenoxyethanol

PEE: phenoxyethoxyethanol

PEG: polyethylenglicol

PEt: polyethylene

1,2 PG: 1, 2-propylene glycol

PLS: partial least squares

POE: polyoxiethylene

Pyr: pyridine

REE's: rare earth elements

Rf: retention factor

RP-HPLC: reversed phase high performance liquid chromatography

RP-IP-HPLC: reversed phase ion pairing high performance liquid chromatography

S: styrene

SALDI: surface assisted laser desorption ionization

SCA: styrene-co-acrylate

SE: solvent extraction

SEM: scanning electron microscopy

SIMS: secondary ion mass spectrometry

SPME: solid phase micro-extraction

SR-FTIR: synchrotron radiation-based Fourier transform infrared

TBA: tributylamine acetate

TBABr: tetrabutylammonium bromide

TD: thermal desorption

TEA: triethanolamine

TEG: triethylene glycol

TLC: thin layer chromatography

TOF: time of flight

TXRF: total reflection X-ray fluorescence

UCH: unsaturated cyclic hydrocarbons

UV: ultra violet

UV-Vis: ultra violet- visible

VSC: video spectral comparator

XRF: X-ray fluorescence

WAXD: wide-angle X-ray diffraction

Abstract

During the last years (2000-2014), many publications concerning the forensic analysis of questioned documents have been published, and new techniques and methodologies are nowadays employed to overcome forensic caseworks. This article reviews a comprehensive collection of the works focused on this issue, dating studies, the analysis of inks from pens and printers, the analysis of paper, the analysis of other samples related to questioned documents and studies on intersecting lines. These sections highlight the most relevant analytical studies

by a wide range of analytical techniques. Separation and spectrometric techniques are critically discussed and compared, emphasizing the advantages and disadvantages of each one. Finally, concluding remarks on the research published are included.

1. Introduction

Regarding the forensic standpoint, the forensic analysis documents presents a real interest, as cases of crimes like falsification, questioned signatures, threatening letters or even terrorist attacks may leave them as evidence. Despite applying pseudoscientific studies as graphology (analysis of handwriting, specially related to human psychology) **[1]**, physical and chemical analyses are more employed. In fact, some reports concerning the analysis of ink through chromatographic and electrophoretic techniques were published in the 90s **[2].** Also, in 2002, a review including optical and physical methods was reported **[3]**. Even manuscripts focused on the analysis of specific samples such as black gel pens are published in the literature **[4]**. Nonetheless, forensic analysis of questioned documents has undergone major improvements and real cases can nowadays be resolved from many analytical perspectives. In 2010 some considerations on ASTM standards 1789-04 and 1422-05, related to the forensic examination of inks, were proposed as proof of this development **[5]**. Differences among writing and printing instruments, analytical techniques and real cases, make the selection of the methodology complex.

According to the literature published during last years, **Figure 1** shows the percentage of published papers according to the sample analysed and the analytical technique employed. Regarding the sample (**Figure 1a)** more than 60% of the publications focalized on pen inks. Printers, paper, intersections and other samples were studied in a lesser extent. In addition, more than 60 % of the studies regarding the analysis of pens are focused on ballpoint pens. On the other hand, almost 70% of the works have studied the differentiation of the ink, whereas the remaining studies focused on dating samples. **Figure 1b** collects the percentage of works as a function of the year and type of analytical technique employed. As can be seen, an increase in the use of spectrometric techniques has been clearly evidenced over the years. With reference to the spectrometric techniques, almost 50% of the studies have employed analytical MS, while the remaining articles focused on other analytical techniques such as IR, Raman or UV-Vis spectroscopy.

Regarding the samples, it is important to acquire a background on the different technologies to interpret correctly the information collected in this review article. Basically, ink is usually a complex homogeneous medium, composed of solvents, pigments, dyes, resins,

lubricants, solubilizers, surfactants, particulate matter, fluorescers, and other materials. This mixture of components, usually under patent, is useful for giving the colour, controlling density or flow, modifying the drying kinetic and providing the final appearance. In particular, colorants play an important role in the ink composition. **Table 1** shows the dyes and pigments found in the articles reviewed. Note that the C.I. name as well as other typical names are provided in the table.

Regarding pen ink and printer technologies, the following classification may be considered. On the one hand, there are three well established pen ink groups in the market. Fountain pens use water-based liquid ink delivered through a nib. The ink flows from a reservoir through a "feed" to the nib, then through the nib, due to capillary action and gravity. Ballpoint pens dispense viscous oil-based ink by rolling a small hard sphere. The ink dries almost immediately on contact with paper. This type of pen is generally inexpensive and has replaced the fountain pen as the most popular tool for everyday writing. Rollerball pens dispense a water-based liquid or gel ink through a ball tip similar to that from ballpoint pens. The less-viscous ink is more easily absorbed by paper than oil-based ink, and the pen moves more easily across a writing surface. On the other hand, printer technologies in the market can be divided as follows. Toner-based printers employ a xerographic printing process but differ from analogue photocopiers in that the image is produced by the direct scanning of a laser beam across the printer's photoreceptor. Liquid inkjet printers operate by propelling variably-sized droplets of liquid or ink. Solid ink printers (phase-change printers), are a type of thermal transfer printer that uses solid sticks of CMYK-coloured ink which are melted. There are other less frequent technologies such as dye-sublimation printers and inkless printers. However, most research has been focused on the two firsts technologies, as toner-based and inkjet printers are the most employed.

Apart from these samples, there are other ones such as the support itself (the paper) or other inks from stamps, as well as more complex documents like receipts, bills or banknotes. Also, more complex systems such as intersections between different inks are of special importance in casework. These different but related samples and cases can be analysed by using different analytical techniques. This review intends to present a comprehensive report on the techniques and methodologies applied during the last years (2000-2014) in the analysis of forensic samples related to questioned documents. Sections focusing on these samples (inks from pens and printers, paper, other samples and studies on intersecting lines) have been described. For ease of the reader, tables have been made describing highlighted information from the articles (samples under study, treatments, techniques, major goals and relevant

information). Abbreviations from text and tables can be consulted in the appendix of the manuscript.

2. Dating studies

Before discussing the most recent literature on ink analysis from different samples, the ageing of samples and relevant studies on this issue are considered due to its importance. Focusing on the bibliography, there are two different but complementary perspectives when analyzing a questioned document. The first one attempts to study ink dating through compounds which degrade over time with the aim of estimating the age of a questioned entry; the second perspective is based on the analysis of the ink composition in order to characterize, identify, or compare between inks or ink strokes.

Ink dating is a challenging issue, as one must take into account that each compound begins to decompose after depositing the ink on the paper through different mechanisms: i) dyes decompose over the time; ii) volatile compounds (solvents) evaporate to the atmosphere and also migrate or diffuse through the paper fibres [6]; iii) resins start to polymerize and strokes become harder. Proof of the diversity of the variety of studies is evidenced in a comprehensive review published in 2010 and focused on the methods for dating ballpoint pen inks during the last 30 years [7].

Here we have attempted to collect only the most recent works regarding the ageing of ink samples on the basis of the analytical technique employed. Note that different writing technologies apart from ballpoint pens have been subjected to ageing studies and have been discussed in the following section. Other samples such as ink from printers, or office paper, have been hardly studied from this standpoint compared to pen ink.

Table 2 summarizes the articles regarding the ageing studies of inks through separation techniques. Both HPLC and GC have been employed, the latter usually coupled to MS. On the contrary, HPTLC has been hardly employed for this purpose [23].

HPLC has been used to detect degradation products from different dyes (with or without identification) focusing on the degradation kinetics of these compounds. Only some resolution

of real casework with controversial results [10] and a comprehensive method validation [11] have been published, while in most of the articles authors studied controlled strokes written on paper. Both natural and artificial ageing processes have been performed. Artificial ageing processes consist of applying heat or light to the sample, simulating and accelerated ageing, in order to establish line tendencies that are finally compared to the tendencies from natural ageing processes. To compare both processes, the relative peak heights of the compounds can be compared [12-14] or different dye ratios, for instance, BV1/BV3 quotients may be calculated [10]. Attending to the samples, black and blue ballpoint pens have been the most studied, although some research about red and black fountain pens [14] and black and blue gel pens [12,13] has been published, being solvent extraction necessary in all cases.

On the contrary, GC has been applied to determine, quantify and study the drying process of solvents contained in the ink, usually PE due to its presence in most of the ballpoint pens [17]. Quantitative studies have been attempted [18, 19], and the use of ratios relating the peak areas of solvents are typical strategies to obtain the absolute age (to establish the age of an ink stroke by itself, without comparing with other strokes) or relative age (by comparing different strokes and estimate the oldest) of ink entries [15]. MS has been the detector employed in most of the cases, although the use of FID has also been reported in the literature [15, 16]. Attending to the samples, specific studies on black and blue ballpoint pens and a lack of studies in other pen technologies is evidenced, being scarce literature focused on black roller ball gel pens, [15, 16]. **Figure 2** shows two graphics where the relative amount of different solvents contained in a ballpoint pen is depicted as a function of the time. As can be seen, both evaporation and diffusion of the solvents are fast during the first hours of exposition, while the relative amount of all the solvents remains almost constant after 2-3 days [20]. Therefore, the quantification of solvents can be useful but limited to the first hours after ink deposition on the support, as after this period the solvent quantity remains almost constant and the age estimation may be questioned. With regard to the sample preparation, GC required also solvent extraction although some methods proposed SPME [19] and thermal desorption [22, 23].

Despite less usual, spectrometric techniques have also been employed in ageing studies, and **Table 3** collects the most recent articles regarding this issue. As can be seen, LDI-MS has been the most employed spectrometric technique, although IR and UV-Vis have also been reported in the literature [15, 28, 31, 32]. Regarding the samples, again blue and black ballpoint pens have been the most analysed, although some research has focused on rollerball and gel pens [13, 15, 30]. Dyes such as BV3 and BV1 have been the analytes under study, but

the degradation processes of other substances in the inks like surfactants or resins have been investigated as well **[30, 31]**.

Regarding the sample preparation, the easy way to ionize dyes from inks and analyse them is one of the advantages of using MS techniques, except when MALDI is employed, where a compatible matrix is required, becoming this step more laborious **[26-28, 30]**. Even new alternatives such as EASI-MS, which allows the analysis under ambient conditions, have also been described for the differentiation of ballpoint pens **[29]**. By using these techniques, the identification of dyes and their degradation products is possible, contrary to separation techniques where standards or complementary techniques are required for identification. When using IR and UV-Vis spectroscopy, a solvent extraction is previously required to analyse the ink and therefore the experiment becomes destructive, as the case of separation techniques **[15, 28, 31]**.

The use of accelerated ageing processes, explained before, has been one of the strategies to estimate the absolute age of an ink stroke. As an example, **Figure 3** shows MS spectra comparing both the artificial and natural ageing degradation processes of a dye from a blue ballpoint pen **[26]**. As can be seen, the decomposition-cascade products are evidenced for both processes. In the artificial ageing of a blue ballpoint pen, the mass spectra of BV3 and their degradation products are detected. In the natural ageing, a similar tendency (degradation products) is observed, despite the fact that samples were totally unknown. Therefore, the use of accelerated ageing process to date inks can be useful in some cases. However, the ink composition and the external factors influence on the ageing process, and for this reason, designing an artificial model similar to the natural may be a challenge **[21, 28]**.

Other samples such as ink from printers have been subjected to ageing studies, though very little amount of literature has been published on this issue. For example, UV-Vis spectroscopy was employed to monitor the degradation of cyan, magenta and yellow inkjet printing inks, obtaining degradation behaviours when storing the samples under natural light, while no degradation was observed under dry and dark conditions. Also, some markers for the cyan ink were found to estimate the age of a sample, though more studies on repeatability, reproducibility and larger sets and longer study times are needed to obtain more reliable results **[33]**. With regard to other samples like paper, studies on its degradation have been performed. For example, the characterization of degradation products of aged samples **[34]** or the degradation behaviour of cellulose **[35, 36]** has been studied. However, these studies have not been applied for forensic purposes, being more useful for cultural heritage.

Considering the influence of the external factors and the huge variety among inks, the study of big batches of samples could be useful to establish solid conclusions [31], instead of employing only few samples [15]. Other literature focused on the dating of ink reveals that the use of statistical tools may be of interest to obtain an objective interpretation of the results [16]. While dating inks through separation techniques has been a useful tool for forensic investigations, there is still a lack in agreement between studies and methodologies [37]. Nowadays, efforts are made in order to establish new methodologies to overcome the dating of inks. New strategies, like the use of dissolution-diffusion rates to create calibration curves to estimate the relative age of a stroke, are proposed [38]. However, these methodologies are valid only under certain conditions and therefore expert reports should contain not only the analyses but also the external conditions and possible factors which may affect to the analytical results. Meanwhile, the use of spectrometric techniques has not resolved the problem of the difficult interpretation of the results due to the complexity of the sample and the external factors that influence the degradation processes.

3. Analysis of inks from pens and printers

3.1. Analysis of pen inks

Despite establishing the age of a document is a useful study, most of the published research deals with the discrimination among ink samples by identifying the main components of each sample and their subsequent comparison. In the early days, these studies were made through measurements of the physical properties of the sample, both to the paper (thickness, texture) and ink (colour). Nowadays some of these techniques, in special optical examination, are common in laboratories, because of their non-destructive character, speed, simplicity and easy interpretation [39]. However, inks can nowadays be optically similar and therefore, during the last years, new techniques are used to improve the discrimination power. In addition, the methodologies employed usually possess a non-destructive character and try to provide objective results compared to classical techniques. However, the use of diverse analytical techniques (classical and new approaches) provide complementary results, being the discrimination more effective [40].

Table 4 summarizes the studies focused on the analysis of the ink composition by separation techniques. Contrary to the studies concerning the age estimation, discrimination of ink samples has been classically performed by TLC [39-58], and more recently HPTLC,

whereas other separation techniques such as HPLC, GC or CE have been used in a lesser extent [12, 14, 40, 55].

TLC has been the classical methodology employed to discriminate among ink samples since the 60s. In the US international ink library, TLC data from hundreds of ink samples has been carried out during the last 50 years [51]. In fact, this technique is sometimes used to confirm the results from other techniques such as UV-Vis, CE, TOF-SIMS, LDI-MS or Raman spectroscopy because TLC has been considered the official method [44]. Regarding the samples, again black and blue ballpoint pens have been the most analysed, and solvent extraction has been the method employed to extract the ink from the paper (using MeOH as solvent in most of the cases). Some authors have analysed gel pens [42], but this analysis is difficult as these samples usually have pigments and other non-soluble substances and therefore TLC cannot provide their separation. Analytes are not usually identified, as discrimination of samples is simply based on comparing plates. However, the spots are supposed to be dyes, which in some cases have been identified because standard dyes have been analysed in the same plate [16, 47]. DP of this technique is usually higher than 90%. Nonetheless, considering that discrimination is based on the qualitative comparison of the spots analysed through different light sources (fluorescence, UV, Visible light) one of the largest problems of TLC has been the non-objectivity of the results and the imprecise quantification of analytes. Even when using scanners with different wavelengths and light modes like Vis, UV, IRR or IRL, results may be subjected to large rate errors [16, 27]. Therefore, recent studies have attempted to develop TLC methods capable of providing non-subjective results and homogeneity in all measures. For example, the use of HPTLC together with scanners as detectors and multivariate statistical analysis may be a promising alternative to achieve objective and automatic results from spots on TLC plates [48-51]. HSI is another recent trend in the discrimination of samples, making the results more objective than those obtained with traditional comparisons without spectral information [45]. Finally, coupling TLC to spectrometric techniques is an interesting alternative to take advantage of both the separation power of TLC and the confirmatory character of MS. As an example, **Figure 4** depicts the MS spectra obtained from TLC plates by using an adequate surface sampling probe. As can be seen, with this coupling quantification of compounds can be achieved, and imaging can support a map where intensity is correlated with both the wavelength employed and the ions identified [52, 54].

Apart from TLC, HPLC, GC and CE have also been employed to differentiate among inks. Ballpoint pens have been the samples under study in most of the cases, but gel and

fountain pens have also been characterized **[12, 14]**. Solvent extraction is again the classical sample preparation in these cases, making the analysis destructive. Finally, despite CE has been widely employed for forensic purposes, few research has been devoted for ink analysis, as can be seen in some recent reviews regarding the analysis of forensic samples by CE **[63-65]**. Compared to other techniques like TLC, CE is faster, more reproducible and fewer sample quantities are needed, although it is also a destructive technique. Generally, two methods (one anionic and other cationic) are required to study both basic and acid dyes contained in ink samples, and dyes must be soluble in the BGE to perform the analysis successfully **[57, 58]**. New methodologies have been optimized to make this technique compatible with MS and use in this way a confirmatory technique to detect the different compounds contained in the ink samples **[59]**. Finally, coupling CE to other spectrometric techniques like SERRS has been carried out. The new interface developed demonstrated acceptable robustness in the results by detecting different dyes in the order of µM concentrations previous optimization of the colloid **[62]**.

As stated in the introduction, spectrometric techniques are being widely employed to study samples related to questioned documents. In this section the methodologies which provide elemental information of ballpoint pen inks will be described. Then, techniques and methods which provide molecular information of this sample will be discussed.

Table 5 collects articles focused on the analysis of pen ink through their elemental composition by spectrometric techniques. As can be seen, techniques which provide elemental information are providing promising results in the forensic field, for example LA-ICP-MS, due to the advantages that they present over other analytical techniques, as can be seen in reviews devoted to this technique **[77]**. Regarding the analysis of inks, techniques such as XRF, INAA, ICP-MS, LIBS, and TOF-SIMS have been successfully employed for the characterization and differentiation of ballpoint pen inks **[66-76]**. Limited literature has been reported with regard to other pen technologies like gel pens **[71]**.

Unlike separation techniques, spectrometric ones can identify and quantify major and trace elements and therefore discrimination of samples is more objective and reliable. Other important advantage are their easy or unrequired sample preparation and minimal sample destruction compared to the treatments needed for separation techniques. Nevertheless, some spectrometric techniques are also destructive, like ICP-MS or ICP-AES which require a dilution and digestion of the sample prior to its analysis **[74]**. Other spectrometric techniques presents disadvantages for the characterization of inks. For instance, spectrofluorometry has been hardly used for these samples, probably because it requires them to possess fluorescent

properties. INAA has also been performed to tag inks, though radioactive materials have to be handled, long analysis times are consumed, and sample preparation is difficult [70].

However, other elemental analyses like XRF have been successfully applied in forensic sciences taking advantage of, for instance, portable instruments [78]. Regarding ink analysis, tagging inks with REE'a has been a common methodology to obtain "security inks", as these elements do not degrade over time and different mixtures can be made in order to obtain unique and genuine samples [68, 69]. Nevertheless, the aim of these studies has not been the characterization or differentiation among commercial samples used in real cases. The use of XRF with differentiation purposes has been carried out, obtaining elemental composition of samples without any sample preparation but with interferences from the support (paper) that should be taken into account for the interpretation of the results. This technique is usually complemented with other spectroscopic analysis to increase the discrimination power, like Raman or IR spectroscopy [66, 67]. As drawbacks, this technique requires the sample to be homogeneous and is expensive.

Other techniques like LIBS and LA-ICP-MS do not require sample preparation and are considered quasi-non-destructive, a real advantage in forensic science [71-73]. Despite providing huge datasets, statistical treatments can be applied in order to minimize the data and obtain clear results. For instance, the proper use of MANOVA analysis to treat the raw data from the LA-ICP-MS equipment provided high DP among blue ballpoint pens and was useful for the resolution of a real casework, as can be seen in **Figure 5**. Different ink strokes from the different parts found in suspected documents were cut and directly analysed in a LA-ICP-MS equipment. As can be seen, works suspected of being written after the original date of the document ('received' and 'cash', in Spanish 'Recibí' and 'efectivo') were successfully clustered in a group different from the remaining inks employed to write the documents [72] Finally, TOF-SIMS has proved to be reliable due to its high capability to discriminate among ink samples through both the elemental and the molecular composition. However, routine analyses would be expensive and therefore it is used only in some cases [75, 76].

Table 6 collects summarizes the studies which employed UV and IR analysis to obtain molecular information of the pen and ink samples under study [31, 32, 40, 44, 46, 56, 66, 79-83]. Visual examination of samples sometimes gives important information and high discrimination power [40]. If using statistical tools like PCA the discrimination can increase but not achieve the higher from other techniques such as TLC or MS [79]. Light examination using VSC, which includes for example IRR or IRL, can be employed obtaining discrimination powers of 90% [89]. Regarding the analysis by UV-Vis, most of the studies have analysed

ballpoint pens. Usually dilution of the sample and/or SE are necessary to acquire the spectra, although in some cases sample preparation is not required and analysis of ink strokes is direct [40]. The main advantage of this technique is its simplicity and real effectiveness to discriminate samples through their dye composition without compound identification. However, this technique usually requires other tools to correctly classify and discriminate the samples. Statistical analyses are used to create databases capable of differentiating samples automatically [80]. Nowadays, the standardization of manufacturing processes make the differentiation among inks a difficult task, and therefore, in addition to optical examination, chemical information is required. Chemical imaging is other complementary tool which has demonstrated higher DP than other classical and powerful techniques in ink discrimination like TLC [44].

On the other hand, IR spectroscopy has been used for the analysis of inks from different pen technologies such as ballpoint, gel or liquid pens [31, 32, 46, 56, 66, 82, 83]. Sample preparation is minimal and usually does not require destruction of the sample, although it depends on the IR mode employed. It requires a fair amount of sample compared to other analytical techniques. In addition, spectra obtained are complex due to the large number of compounds that absorb in the same range of the IR spectrum, so discrimination is based on comparison of spectra or fingerprinting of each sample, instead of identifying and quantifying the compounds. Most of the studies however focused on the dye composition, although in some cases chemical groups from other substances contained in inks such as resins or binders have been identified [31, 82]. Similar to the case of UV-Vis studies, statistical tools improve the results obtained becoming them more objective. Advanced and modern techniques like HSI are being recently used because high discrimination power is achieved by carrying out easy analysis without sample destruction, though software and proper statistical tools are also required to overcome the analysis [81].

Undoubtedly, Raman spectroscopy is a complementary technique to IR for the analysis of ink samples, mainly because their principles provide different analytical information. IR can detect the ink matrix (binders, organic additives) and dye composition, whereas Raman is capable of identifying pigments present in gel pens and rollerball pens. Regarding the analysis of questioned documents by Raman spectroscopy, a comprehensive review was recently published [90]. From that review, less than 10 articles on pen ink analysis by Raman spectroscopy were published during the last decade, including ballpoint pens [35, 91, 92] and gel pens [84, 89]. However, comprehensive studies on different pen technologies including ballpoint, fluid and gel pens of different colours and brands had been previously investigated

[85, 86]. The use of combined Raman with other complementary techniques like LIBS has been published [84, 93]. More recently, application of gold cluster coatings to enhance Raman scattering from surfaces has been achieved, concluding that the discrimination power was higher when using SERS [87]. Finally, liquid and gel inks have also been analysed by Raman and SERS. Results showed that Raman was more effective for pigment-based samples while the discrimination power was higher for SERS when studying dye-based samples. However, the discrimination power was poorer for these spectrometric approaches if compared to TLC analysis, although analysis by Raman spectroscopy was necessary for non-soluble inks where TLC cannot provide analytical results [88].

Table 7 summarizes the studies concerning identification and differentiation of pen inks through analytical MS which provides molecular information of the ink under study [27, 29, 30, 41, 76, 94-106]. Regarding the samples, ballpoint pens have been analysed through this technique, and even creation of databases has been proposed in the literature, useful in caseworks [94]. However, these techniques are capable of analysing successfully other non-ballpoint pens like, rollerball pens [95] or gel pens [30, 95, 97, 99, 104] or liquid pen [101, 104], as well as unidentified inks from old documents [96]. Usually dyes are determined, but also other components contained in the formulations like surfactants [30], carriers or resins [104] have been determined.

When using ESI-MS, sample must be diluted in a solvent and solvent extraction is the most employed procedure, although little amount of sample is needed and therefore the method is less destructive than separation techniques. ESI-MS is also fast and reliable and identification as well as calculation of the relative amount of each compounds possible However these spectra may involve mixtures of compounds and sometimes quantification is not possible [94, 95].

LD-MS is non-destructive, it does not require sample preparation, and a soft ionization allows to determine dyes as well as pigments, depending on the wavelength used. For this reason both ballpoint pens, gel pens and liquid pens have been analysed. Positive mode is more studied since most of the dyes form cationic species, but negative mode can provide interesting result in some cases [98]. The characterization of pens by using photodegradation mechanisms to differentiate among samples has been used [107], as well as the characterization of samples through pigments, which do not degrade over time [97]. To improve results and increase the discrimination power of the technique, a matrix can be added to the sample, although it requires a sample preparation and the election of an appropriate matrix (for example DAHC as additive and HABA as matrix), being the analysis more expensive and time consuming [27,

101, 108]. The use of gold nanoparticles deposited on the ink stroke has provided differentiation between inks without sample destruction **[94]**.

TOF-SIMS is another option to analyse ink on questioned documents. Despite only 2 works have focused on this technique to analyse ballpoint pens in the positive mode, its possibility of measuring both elemental and molecular information is of great interest, as commented before. In addition, TOF-SIMS has also provided better results if combining with statistics. However, routine analysis in caseworks would be more expensive and time consuming than the official techniques employed for ink examination and therefore its use is limited only to specific and complex caseworks **[76, 103]**.

Finally, current trends in MS have focused on developing new modes which allow analysis under ambient conditions. These developments have also been applied to discriminate inks, obtaining promising results. For example, DART-MS provides spectra richer than ESI-MS, as other compounds can be identified, although spectra vary as a function of the position analyzed [**104**]. DESI-MS methods have been optimized and coupled to imaging, obtaining spectral images as a function of the ionic composition, and have been successfully applied to discriminate writings on documents. As an example, **Figure 6** shows the differentiation of two inks in a number from a document where some digits had been forged. Therefore, by coupling imaging and DESI-MS spectral information is obtained from an image [**105, 106].**

Electron probe techniques, such as SEM, have hardly been used in the forensic examination of ink samples, and are usually employed together with other techniques like FLE and Raman spectroscopy for the characterization and even creation of databases [**89**].

3.2. Analysis of printer inks

During the last years an increase in the sales of printers has been unquestionable. Some data collected from the literature endorse this fact: in 2002 74 million printers were sold over the world, 5000 real cases where a machine had been used for counterfeiting were reported in Japan **[1]**, in 2008 59% of falsification cases were made with printers in Poland **[109]**. This fact is due to the decrease of the price of printers and photocopier machines, causing their massive use by companies, workplaces and private properties, but also from criminals who use them to counterfeit documents. The new printing technologies provide copies very similar to the original documents, increasing the problem of forgery.

Various analytical techniques have been employed to attempt to discriminate them, apart from other non-analytical techniques, such as the analysis of marks produced by printers or

defects that a particular printer can present [1, 110, 111]. **Table 8** summarizes the research focused on the analysis of printer technologies by analytical techniques.

Different separation techniques have been employed to study samples like toner and inkjet inks. In some cases, sample is extracted directly from the cartridge and sometimes the sample is analysed from the paper, although most studies performed need a sample preparation and they are destructive techniques except. As expected, the characterization of the samples and the discrimination has been carried out without compound identification, considering the extremely complex composition of inks from printers and photocopiers and the limits of separation techniques. Discrimination of samples and identification of compounds, manufacturers or models have been then carried out through comparison of plates, chromatograms or electropherograms. Nonetheless, laser Py-GC-MS has identified AB, furans, phenols and unsaturated cyclic hydrocarbons in black and colour toners, although with no reproducibility [114]. Databases have been created [112], and the use of statistic tools seems a current trend for the reliable differentiation of samples [114].

Spectrometric techniques have also been employed for the characterization of black and color inks from toners and inkjet cartridges. Here sample preparation is simpler, or even not necessary. Identification and quantification of compounds is not usual, because comparison of spectra is enough to discriminate among samples. However, in some works elements (Fe, S, Cr, Cu) and compounds like dyes (TAM, CBl, BV3, SBl) or other additives (PEG, S, Ac, TiO_2, OA) have been identified.

Regarding IR and Raman, spectral databases have been successfully created and employed to establish the relationship between a sample and a model, brand or manufacturer. Clustering into groups can be made through the top hits (characteristic peaks in the spectra of different samples). **Figure 7** shows as example different IR spectra from the most typical resins found in photocopy toners, which can be used to create a spectral library [122]. To measure the samples, ink may be transferred from the paper to an Al foil via soldering, and samples remain legible after the process. In addition, just as the case of the analysis of pens, these techniques can complement one another, as IR provides matrix ink information (polymers and resins) [114, 121, 122, 124-126] while Raman can identify pigments [88, 124, 120].

Various modes of analytical MS have been used as well. The main advantage of these techniques is the possibility of detecting the compounds contained in the sample, such as polymers, resins, alcohols, dyes and pigments.

4. Analysis of paper

As important as the ink itself, the support where it has been deposited can be a significant evidence in a crime, as some elemental differences can be identified when studying different paper sources. The amount of paper that is made is immense, and therefore their production is in batches. The paper is made from cellulose and hemicellulose from wood. In order to form the pulp, it is indispensable to remove lignin which is the compound that holds the hydrocarbons. Both in the pulping process (usually the Kraft process) and in the process of bleaching, chemical compounds are introduced, like Na_2S or $NaOH$, Cl_2O, $CaCO_3$, ozone or oxygen along with metallic oxides, these agents cause the finished product. Then the product has, besides cellulose, certain compounds characteristic of each production [132].

Physical properties like strength, thickness, color, fiber content, fluorescence or mass/area can be measured to compare different sheets of paper. These comparisons are both inexpensive and easy to perform, but the manufacturing of the sheets of paper makes them really homogeneous and even batches from different manufacturers in different countries can be very similar physically. In addition, physical test are sometimes destructive. However, taking advantage of the composition of the document papers, it is possible to characterize them through their trace elements, which can be different from one manufacturer to another.

X-ray techniques have been used for this purpose [132-134]. ED-XRF has been used to determine the elemental composition of paper. In one of the works, the authors attempted to develop a reliable and non-destructive method to discriminate paper sheets for forensic purposes through a combination of ED-XRF and MS techniques [133]. 25 samples of paper were measured, picking up three different areas within the sheet to measure also the internal variability. ED-XRF was able to measure thirteen elements, and PCA was applied in order to reduce variables. With CA 22 of the 23 samples could be differentiated. In addition elemental contribution of components was showed through ED-XRF, demonstrating the high contribution of Sulphur. With MS, every sample could be distinguished. However, batch discrimination was not entirely successful.

ICP-MS has been the most employed technique used in the last decade, either by itself [135-137] or complemented with other techniques [71, 133]. The advantages of ICP-MS are: speed, quantitative and multi-elemental analysis, high sensitivity and precision. However this technique is destructive and in some cases the destruction of the sample must be avoided. As well as for the ink samples, paper sheets need a treatment before measuring with ICP-MS, which is usually a microwave digestion with HNO_3. Afterwards, inorganic elements are

identified and quantified. It should be clear that the most discriminating elements were selected for discrimination For example, 17 samples of different countries were studied by selecting Mn, Sr, and Al as PCs and achieving the differentiation of all samples **[135]**. The potential of ICP-MS to discriminate within batches, between batches and between vendors has also been studied. Within a batch ICP-MS did not found significant differences, whereas the discrimination was partial between batches. Between vendors differences were clear **[137]**.

More recently, LA-ICP-MS has been employed for paper characterization, which maintain the advantages of ICP-MS, but the laser makes it a quasi-non-destructive technique, and therefore, as discussed in the analysis of ink samples, a previous digestion is not required. In one of the works 25 samples were analyzed and 51 elements and isotopes were detected. With PCA 23 of 25 samples could be differentiated. They also complemented the technique with Isotope Ratio-Mass Spectrometry (IRMS) **[133]**. Latterly in other attempt, 17 different samples were studied, and 99.6% of DP was obtained, even with batches from the same manufacturer. The DP of LIBS was also calculated (97.7%) **[71]**. Finally, DART-MS has also been employed to characterize and discriminate paper samples **[138].**

Wide Angle X-Ray Diffraction (WAXD) has been used because of the advantages this technique presents: measuring both the degree of crystallinity of cellulose (structural information) and the inorganic formulation added to the paper sheets by the manufacturers is possible. The authors studied 19 samples physically similar, revealing that: cellulose type I and II are the most common in paper sheets and cellulose structure is a mixture of amorphous and crystalline polymer. 95.3% of the pairs of samples could be distinguished. $CaCO_3$ and other minority additives could be detected (useful to discriminate between samples). Within the sheet the composition was almost homogeneous. Using FTIR as a complementary technique, areas of cellulose and $CaCO_3$ could be quantified and all samples were differentiated **[134]**.

5. Analysis of other samples related to questioned documents

Throughout the manuscript studies based on the analysis of the most important samples in document examination, pen technologies, printer technologies and paper have been showed and discussed. However, other samples have been analyzed through different analytical techniques as they are involved in criminal acts.

Stamp and sealing inks have been analyzed through both separation and spectrometric techniques. For example, MECC-DAD and CZE-MS have been employed for the examination of color stamp inks for forensic purposes, being the only research that uses CE as separation

technique for the characterization of these samples, where 10 different brands of 4 different colors were analyzed (38 samples). The MECC-DAD method provided irreproducible migration times and relative times were used to obtain low RSDs (from 0.86 to 3.64%). Green inks were completely differentiated, whereas blue samples were the most difficult and UV-Vis spectroscopy was needed for a better discrimination. Blue and violet samples were subjected to CZE-MS as the MECC method was not discriminating enough, and a higher DP was obtained, although the methodology is more complex and the equipment more expensive [139]. Regarding the spectrometric techniques. µ-ATR-FTIR was used to study documents involving red seal inks. Through a database, the aim of the study was to determine the origin of the ink. For this purpose, samples without previous treatment were analyzed separately and paper interference spectra was suppressed. Seals from the same color and different manufacturer were successfully determined, even with old documents dated from 1997 [140]. The combination of Raman and FTIR is again a good alternative for the characterization of inks, in this case red ink entries of seals. 105 samples were analyzed with these non-destructive techniques, and paper spectra were subtracted as well. The set of samples was clustered in 4 groups through their Raman spectra. After, each cluster was subjected to FTIR and different subgroups were created. At the end 70 inks were individualized, and the remaining 35 were clustered in 13 subgroups, achieving a DP of 99% if combining both techniques [141]. Nevertheless, Raman spectroscopy may provide enough information to characterize these kind of samples. Recently, this technique was used to study stamp inks. 9 blue stamping inks were directly analyzed without sample preparation and clustered in 5 different groups, obtaining a DP higher than that from the TLC analysis [142]. Finally, MS has also been used to characterize red sealing inks. In the study, TOF-SIMS was employed to determine the elemental composition of 5 samples. Ca, Pb, Zn, Ba, Cl⁻ and I⁻ were detected by using a quasi-non-destructive methodology, allowing the characterization of the samples [143].

Checks and banknotes have been studied in a lesser extent. For their characterization, spectrometric techniques and more specifically IR and Raman spectroscopy have been employed. FTIR has been applied to characterize check paper. The authors studied the vibrational conduct of cellulose via computational method (*Ab initio* HF/6-31G (d)), obtaining infra-red (IR) and Raman spectra as well as vibrational numbers. Comparing with experimental analysis, they noticed a relationship between the intensity of C=O peak and the degradation of the paper, and some dyes were identified via the IR spectra [144]. Discrimination between authentic and counterfeit Brazilian banknotes was successfully achieved by using Raman spectroscopy and PLS-DA which provide the uncertainty of the results obtained [145]. µ-

Raman spectroscopy has also been used to identify a common origin of toner printed counterfeit banknotes **[146]**. Few studies on these types of sample have been published **[147, 148]**, in the literature, and only one work described the use of LDI-MS and molecular imaging to characterize banknotes **[102]**.

Plastic cards, photos and printer ribbons have been analyzed through TLC. After extraction with pyridine and TLC analysis, resulting spots were measured using UV light and a VSC, obtaining a fast and reproducible methodology to discriminate among samples. Databases were created through this method **[149]**.

The elemental analysis of **pencil marks** has also been performed. Authors used ICP-MS and TOF-SIMS for the discrimination of pencil markings (11 samples). ICP-MS analysis evidenced homogeneous composition along the lead and discrimination between all brands. TOF-SIMS analysis could differentiate all brands and batches with PCA analysis **[150]**.

6. Recent studies on intersecting lines

As can be seen, a wide range of samples involved in questioned documents have been studied for forensic purposes. However, in many documents there are not only one kind of ink, and **intersecting lines** or combination of inks are present on the paper. It is important to highlight that recently, the sequencing of intersecting lines is being studied as it provides useful information in forensic caseworks. This trend is also possible due to the improvements of the analytical techniques, which allow the correct sequencing of intersections.

The potential of the 3D micro-topography has been showed in the study of the sequence of intersecting lines. In most of the cases a correct order sequence was obtained. In addition, intersections of two mixed inks of similar color was also successfully achieved **[151]**. DocuCentre expert and PIA-600 software have been used to study the intersections between intersecting printed strokes with writing instruments, but this technique was not useful for the correct determination of the sequence of intersecting lines **[152]**. The same kind of intersections were tested by using VSC. Laser printers (black, blue, red and green) and black typewriter ink with strokes of gel pen ink, ballpoint pen and fountain pen (black, blue, red and green) were evaluated. Again, signals from printers and typewriters prevailed over the pen inks and therefore inconclusive results were found, advising against the use of this equipment for the study of intersection lines **[153]**.

ATR-FTIR imaging was used to obtain the sequence of writing lines between printer and ballpoint pen intersections. Results showed the high absorbance of toner in comparison to

ballpoint pens. Blind tests were made and 100% correct results were obtained. However, this methodology was inappropriate for inkjet, roller ball and gel pens **[154]**. μ-ATR-FTIR has been used to study the intersection between red-sealing inks and black ballpoint pens. By relating characteristic peaks of each sample to the signal of the intersection obtained, the correct order of deposition was successfully achieved **[140]**. FTIR was also combined with SEM-EDS mapping for the sequence of laser toner and seal ink, obtaining higher accuracy in the results. Elemental distribution in the intersection was calculated, making the results more reliable **[155]**.

Regarding Raman spectroscopy, it has been used to analyse intersections of different writing instruments and printers (ballpoint pens, fibre tip pens and roller ball pens, and also 5 different inkjet printers). Only 54.9 % of positive results for heterogeneous intersections (made with different writing technologies) and 29.1 % for homogeneous intersections (made with the same writing technologies) were achieved, leading to many misleading results and concluding that the technique was not capable of giving a high rate of correct results **[156]**. However, in other recent study, Raman spectroscopy was used to determine the order of sequence of lines from different red stamps with pencil, printer ink, red gel inks and red ballpoint pens. The order of sequence was determined by comparing the Raman spectra of the intersection with those from the inks alone **[142]**.

If using TOF-SIMS in the negative mode, the sequence of red sealing inks and black ballpoint pen can be achieved **[143]**. TOF-SIMS has also been used to determine the deposition order of latent fingerprints and ink from a pen. In this case, to determine the order, characteristic ions from the ink were determined and SD of the intensity variation across the line scan were measured **[157]**. TOF-SIMS chemical mapping was also used to study the order of deposition of latent fingerprints and laser printed ink. Taking in this case Na, K and C_3H_5 positive ions (present in both the paper and the fingerprint but not in the ink) the correct order of deposition was obtained in 100% of the blind tests performed. Ageing of the sample did not compromise the results **[158]**.

7. Concluding remarks and future trends

Taking into account the literature published up to date, there is an increasing in the use of non-destructive spectroscopic techniques, since they provide useful, specific and complete information without damaging the sample (or causing minimal damages). Among the characteristics that an analytical technique can possess, the non-destructive character is one

highly important in the forensic field. Therefore, destructive techniques are used after non-destructive instrumentation. Among the non-destructive techniques, IR, Raman, hyperspectral imaging, and quasi non-destructive LIBS and different modes of MS (LA-ICP-MC, ESI-MS) are being widely employed with promising results.

Most of the published literature has focused on the analysis of the most typical sample, blue ballpoint pens, whereas the analysis of printers, paper, and other samples and intersecting lines have been studied in a lesser extent. For this reason, developments in the analysis of ballpoint pens of other colours, as well as non-ballpoint pens and other technologies could be of great importance in some casework. On the other hand, the characterization of the samples considering other compounds different from dyes or pigments (e.g. solvents, polymers, resins, etc) is open to be investigated to support the previous literature and complement the current discrimination power based mostly on dye differentiation.

Dating studies on ballpoint pens have, as a general rule, some disadvantages, like the need for analysing patterns to identify compounds and their subproducts, or the fast evaporation of solvents which makes difficult the dating of relatively old documents (some months of age). Heat or light accelerating methods are sometimes useful but kinetics are still unknown and depending on the conditions the results and subsequent interpretation might vary significantly. In addition, external and ungovernable factors (environmental conditions, stroke thickness, cross-contamination, paper used, under-patent formulations, etc) affect to the results obtained. As consequence, dating studies are of special importance in document casework. It is however a challenging issue that needs a further development to achieve a better understanding of the ageing processes and establish more specific results.

On the other hand, the characterization of ink composition has been achieved by both separation and spectrometric techniques, obtaining more robust results than those from dating studies. TLC interpretation is usually performed without identification, showing a high discrimination power in all of the studies. When comparing different techniques, TLC has been necessary in some cases where other techniques were not able to discriminate among certain pairs. In other cases, however, pairs easily distinguished with other techniques have not been discriminated by TLC, so this technique is not 100% effective. Coupling separation techniques with MS provide higher DPs.

Some spectrometric techniques provide the elemental information of the samples, but sometimes require sample destruction. Nevertheless, new techniques such as LA-ICP-MS or LIBS are quasi-non-destructive, allowing higher DPs, despite being quite expensive.

Techniques capable of detecting the molecular composition of the ink samples have been also employed, usually without compound identification. Most of these techniques in addition require minimal sample preparation. IR and Raman spectroscopy are complementary techniques and can be used to detect different compounds from the same sample, obtaining high DPs if combining both techniques. In addition, they allow the subsequent analysis by other techniques as they may analyse samples in non-destructive way.

Analytical MS is probably the most employed spectrometric technique. Reliable and objective characterization of samples is achieved, and it can be complemented with statistical tools and other analytical techniques, obtaining promising results. However, their implementation in routine analysis is limited due to the complexity and high price compared to other techniques like optical examination or official methodologies based on TLC analysis.

With regard to the analysis of inks from printers, it is important to highlight that the composition is usually more complex, containing a wide variety of compounds and usually presenting more pigments and polymers (up to 80% of the composition) than inks from pens. The identification of every signal is not necessary, and samples can be classified in groups to create a library. Analysis of cartridges and samples printed on the paper provided almost equal results, except in some cases where cellulose peaks are present due to the interferences from paper sheets. Differentiating between samples produced by the same manufacturer for the same model is the most complicated task. Samples from the same manufacturer but different model are easier to distinguish, and samples produced by different manufacturers are almost always identified because of the large number of differences in composition. Each technique provides different useful information and there are no a clear trend in one kind of methodology or technique. However, multivariate statistical analysis is in all cases useful due to the ease of interpreting results, reliability and speed if there are a significant number of samples.

Other samples related to questioned documents, such as papers, pencils, ink from seals, and studies on the intersection of lines have also been collected, being the study of intersection lines a current challenge where further research is needed. Spectrometric techniques are becoming more important, possibly because most of them are not destructive, and can identify and quantify compounds and elements easier than separation techniques. Moreover, ageing studies can be performed with these techniques since dye degradation products can also be identified. However, the use of different separation and spectrometric techniques provides complementary and more realistic results.

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Figure 1. Analysis of the articles recovered from the literature during the last years focused on the analysis of questioned documents. a) pie chart with the distribution of articles as a function of the sample under study; b) bar chart with the trend of the use of separation and spectrometric techniques over the last decade.

Figure 2. Example of ageing curves from different solvents from Parker ballpoint pen entries. E = ethoxyethoxyethanol; D = dipropylene glycol; P = phenoxyethanol; PE = phenoxyethoxyethanol. a) relative peak areas of solvent to the IS as a function of the square root of the time in hours, b) relative peak areas as a function of time on a double logarithm scale. Figure taken from [20] with permissions of Elsevier.

Figure 3. Mass spectra from a Bic blue ballpoint pen. a) UV aging study, with mass spectra at different hours showing the degradation products cascade. b) natural aging study from three different documents dated in different years. Figure modified from [26] with permissions of Elsevier.

Figure 4. Identification of spots from TLC plates by using an adequate interface for TLC- MS coupling. a) TLC plate with three different dyes and their mixture; b) methylene blue (SB9), c) crystal violet (BV3); d) rhodamine 6g (BR1). Figure modified from [53] with permissions of ACS publications.

Figure 5. LA-ICP-MS analysis of a real questioned document with blue ballpoint pen strokes. On the left the questioned document with the selected fragments to be analysed (text, number, questioned ink entries and signature). On the right the resulting PCA analysis. Figure modified from [72] with permissions of Elsevier.

Figure 6. DESI-MS can differentiate between 2 different inks in a forged number (A). As can be seen, the middle numbers (98) contain the dye SB2 (spectrum B), whereas extreme numbers (1-2) contain the dye BV3 (spectrum C). Possibly, middle number had been manipulated. Figure taken from [105] with permissions of RSC publishing.

Figure 7. Analysis of printers. Spectra of major resin types found in photocopy toners: A polystyrene; B polystyrene-co-acrylate; C polystyrene-co-acrylate with Prussian blue; D epoxy; E epoxy plus acrylate; F poly-ethylene; and, G polyethylene with an additive, possibly SiO_2. Figure taken from [122] with permissions of Springer.

Table 1. List of dyes according to their abbreviation. C.I. generic names and other common names are given.

Abbreviation	C.I. generic name	Common names[a]
AB1	Acid blue 1	Blue violet, Patent Blue VF
AB49	Acid blue 49	-
AB9	Acid blue 9	Brilliant blue FCF
AB9	Acid blue 9	FD&C Blue no. 1 (6, brilliant blue FCF,)
AB90	Acid blue 90	-
ABl1	Acid black 1	Naphthalene black 12B
AO7	Acid orange 7	Orange II, Tropaeolin OOO
AR52	Acid red 52	Sulforhodamine B
AR92	Acid red 92	-
AGs	-	Arylguanidines
AY23	Acid yellow 23	Tartrazine, food yellow 4
AY36	Acid yellow 36	Metanil yellow
AY42	Acid yellow 42	Acid Yellow FG
BB11	Basic blue 11	Victoria blue R
BB12	Basic blue 12	Nile blue A
BB17	Basic blue 17	Toluidine blue O
BB26	Basic blue 26	Victoria blue B
BB3	Basic blue 3	Solvent blue 3
BB7	Basic blue 7	Victoria Blue Pure BO
BB8	Basic blue 8	Victoria blue 4R
BB9	Basic blue 9	-
BCB	-	Brilliant blue C
BR1	Basic red 1	Rhodamine 6G
BR9	Basic red 9	Pararosaniline
BV1	Basic violet 1	Methyl violet, gentian violet
BV10	Basic violet 10	Rhodamine B
BV14	Basic violet 14	Fuchsin Rosanilin
BV2	Basic violet 2	New fuchsin
BV3	Basic violet 3	Crystal violet
BV4	Basic violet 4	Ethyl violet
DDG	-	1, 3-dimethyl-1, 3-ditolylguanidine.3
FG3	Food green 3	Fast green FCF
FY3	Food yellow 3	Sunset yellow FCF
Gu	-	Guanidine

PB122	Pigment blue 122	-
PB15	Pigment blue 15	Phthalocyanine blue
PB17	Pigment blue 17	Cu phthalocyanine
PBk7	-	Carbon black
PO13	Pigment orange 13	-
PR12	Pigment red 12	-
PR15	Pigment red 15	-
PV23	Pigment violet 23	-
PY12	Pigment yellow 12	-
R123	Rhodamine 123	-
RB31	Reactive black 31	Dinazol Black RL
SB2	Solvent blue 7	-
SB7	Solvent blue 7	-
SB21	Solvent blue 21	-
SB23	Solvent blue 23	-
SB38	Solvent blue 38	Fast blue MBSN
SB8	Solvent blue 8	Methylene blue
SB9	Solvent blue 9	Methylene blue
SBl27	Solvent black 27	-
SBl3	Solvent black 3	Sudan black B
SBr20	Solvent brown 20	-
SO3	Solvent Orange 3	-
SO3	Solvent orange 3	Chrysoidine Y Base
SV49	Solvent violet 49	Rhodamine base B
SY19	Solvent Yellow 19	-
SY47	Solvent yellow 47	Sepisol fast yellow TN
SY49	Solvent Yellow 49	-
SY94	Solvent Yellow 94	Fluorescein
TAM	-	Triarylmethane

[a] Hyphen indicates that, despite the existence of other common names, those were not found in the literature reviewed.

Table 2. Studies on ink dating by separation techniques.

Sample(n)	Sample prep	Analyte[a] [compound]	Technique-Detector		Goal	Relevant information	Ref.
Ballpoint Pen (1 blue)	SE (MeOH)	BV3, BV1, BR9 [dyes]	RP-HPLC	DAD	Degradation in light / darkness	Result: composition changes at light (less in darkness) due to the light. Ternary diagrams showed linear degradation (during 2 years).	[8]
						Conclusion: useful for entries in chronological order. Environmental conditions distort results.	[9]
Ballpoint pen (1 blue)	SE (MeOH)	BV3, BV1, BR9 [dyes]			Dating in real case	Result: inks differentiated through ratio BV3/BV1 Conclusion: no deliberate misrepresentation.	[10]
Std. Dye (5) Ballpoint pen (3 blue) (3 black)	SE (AcN) Sonication	AB1, BV14, BR9, BV3, BB26 [dyes]			Method validation	Result: r > 0.996, RSD < 10%, LOQ = 0.2-6 ng. Logarithmic degradation of BV (during 1.5years). Conclusion: useful method for relative ageing. More samples should be studied.	[11]
Gel pen (50 black)	SE (TBABr /AcN 40:60)	- [dyes]	RP-IP-HPLC	UV	Artificial/ natural ageing	Result: 40mmol TBABr, pH 7.0 (optimized). Natural ageing slower than artificial (0.5-1year). Conclusion: useful to identify light-treated samples. Degradation depends on ageing conditions.	[12]
Gel pen (27 blue)	SE (TBA /AcN (1:1))	AB9 [dyes]			Light/natural ageing mechanisms	Result: 10mmol TBA, pH 7.0, optimized conditions. Natural ageing slower than artificial. Conclusion: Useful to date samples (0.5-1year).	[13]
Fountain pen (12 black) (6 red)	SE (TBABr /AcN (1:1))	- [dyes]				Result: 40mmol TBABr, pH 7.0 (optimized). Ink degraded linearly with time. Conclusion: Useful to date samples (2-3years).	[14]
Roller ball and Gel pen (6 black)	SE (MeOH, DMF)	- [dyes] [solvents]	GC	FID	Relative and absolute ageing	Result: peak areas and Peak ratios to study ageing. Conclusion: relative (0.5-1year) and absolute (90 days maximum) ageing possible but not accurate.	[15]
Gel pen (30 black)	SE (MeOH)	1,2 PG,DEG,EG, G [solvents]			Light/natural ageing	Result: 4 groups classified. Dating after 100 days (natural ageing) or 2-4 h (UV ageing) not possible. Conclusion: Reproducible, valid for relative ageing	[16]
Ballpoint pen (279 black) (354 blue)	SE (AcN)	PE, DGPE [solvents]			Identification of 2-PE	Result: PE in 85% and 83% of black and blue samples. DGPE present in 21.5% and 12.1%. Conclusion: GC-MS useful to quantify PE.	[17]
Ballpoint pen (2 blue)	SE CCl3/pyrTFA(5:1:1)	PE, nonadecane [solvents]			Quantification of 2-PE	Result: ratios (using a stable IS, nonadecane) remained stable after 1 day. Conclusion: dating was not possible. A theoretical study of ink degradation is given.	[18]
Ballpoint pen (1 black)	SPME	BA, PE, NMP [solvents]			Quantification of solvents	Result: SPME effective and non-destructive. Conclusion: differences between samples with more /less than 6 months old.	[19]
Ballpoint pen (12 blue)	SE (DCM)	DEGEE,DPG PE,PEE [solvents, resins]		MS	Drying process of ballpoint pens	Result: 54% of ink is solvent (PE in 94% of cases). Conclusion: Differentiation of inks younger than 2 weeks. Degradation depends on the solvent.	[20]
Ballpoint pen (2 blue)	SE (DCM)				Artificial/ natural ageing	Result: light and its intensity affects to the process Conclusion: Differences in artificial/natural process	[21]
Ballpoint pen (85 blackblue)	TD	PE [solvents]			Age determination	Result: general procedure assessed. Ratios to obtain mass independent results. Conclusion: sample and temperature influence	[22]
Ballpoint pen (13 colour unknown)		PE [solvents]			Variation of ref. [22]	Result: Fast/slow ageing samples distinguished. Conclusion: similar artificial/natural ageing processes.	[23]

[a] hyphen indicates that the dyes were not identified.

Table 3. Studies on ink dating by spectrometric techniques.

Sample (n)	Analyte[a] [compound]	Technique	Goal	Relevant information	Ref.
Old pens 5-20 years old	BV3, BV1 [dyes]	LD-TOF-MS	Degradation of ink inside a cartridge	Result: ageing influenced by ink composition (degradation in some cases). Conclusion: technique sensitive enough to date samples.	[24]
Ballpoint pen (1 blue) (1 black)		LD-TOF-MS	Dating questioned documents	Result: faster degradation in blue than in black pens for BV1, paper influenced. Conclusion: BV3 degrades via oxidative demethylation. Fast, sensitive and non-destructive technique.	[25]
Old documents Ballpoint Pen	BV3, BV1 (black,blue). BV10, BR1 (red) [dyes]	MALDI-MS	Dating documents using accelerated processes	Result: presence of degradation products (more in old documents). Same spectra 0, 12, 24h of irradiation. Conclusion: technique suitable for dating ballpoint pens. Accelerated processes useful and similar to natural.	[26]
Ballpoint pen (1blue)	BV1, BV4 [dyes]	LDI-TOF-MS MALDI-TOF-MS	Factors influencing degradation	Result: BV3 less stable than BV1. Conclusion: sample treatment, laser (intensity and wavelength), matrix (DHB) and humidity influenced degradation.	[27]
Ballpoint pen (4 blue)	BB3 [dyes]	MALDI-TOF-MS UV-Vis LDI-MS	Influence of the ink components in the dye degradation	Result: different degradation mechanisms as a function of the matrix. Stroke thickness influences on the degradation. Conclusion: ink composition influences on the ageing.	[28]
Std. dyes (1) Ballpoint pen (2 blue)	BV4 [dyes]	LDI-TOF-MS	Artificial/natural ageing	Result: dye degradation more complex than solvent drying. Dating affected by ink formulation and light. Conclusion: modelling an artificial process is difficult (influence of too many factors).	[21]
Gel pen (47 blue)	AB9 [dyes]	ESI-MS/MS	Degradation studies of inks	Result: similar UV and fluorescent light degradation. AB9 identified. One compound unidentified.	[13]
Ballpoint pen (red, blue) Old documents	BV3. BB26, BB7, NP, DDG (blue). BV10, BR1 (red) [dyes]	EASI-MS	Fingerprinting of inks samples	Result: fingerprinting was successful. BV3 was identified in all the blue ballpoint pens. Conclusion: fast and non-destructive method. Superficial information.	[29]
Gel pens (40 black) (5 blue)	BB7, BV10 (blue) BB26 (black) [dyes] POE, PEG [surfactants]	MALDI-TOF-MS	Dating gel pens	Result: HPLC-QTOF-MS and TLC to detect dyes. UV and natural degradation linear with time. Fluorescent light degradation nonlinear and weaker. 20% degradation of BB7 after 5 years. Conclusion: technique capable of discriminating and dating gel samples.	[30]
Ballpoint pen (108 blue)	TAM [dyes] ER, AlR [resins]	FTIR	Influence of the time in the IR spectra	Result: IR spectra change with time, heat and light. Changes depend on ink composition. Relative height peaks to estimate the age. Conclusion: fast reliable and non-destructive analysis.	[31]
Ballpoint pen (10 blue)	BV1, BV3 [dyes]	UV-Vis IR	Potential of PCA in the analysis of inks	Result: UV-Vis spectra change with time in dark and normal conditions. Correlation lines to estimate age. Conclusions: dating is not always possible.	[32]

Rollerball and gel pen (6 black)	- [dyes]	UV-Vis	Absolute and relative age of samples	Result: ratios based on peak areas allow age determination. Conclusion: effective method. Few samples are analysed.	[15]

[a] hyphen indicates that the dyes were not identified.

Table 4. Studies on ink composition by separation techniques

Sample (n)	Sample prep.	Analyte[a] [compound]	Technique	Detector	Goal	Relevant information	Ref.
Ballpoint pen (16 blue)	SE (3 systems)	- [dyes]	TLC	UV	Differentiation, Technique comparison	Results: 115/126 samples distinguished (95.8%). Extractant and elution solution optimized. Conclusion: TLC higher DP than other techniques.	[40]
Gel pen (29 black)	SE (EtOH:H$_2$O 1:1)	- [dyes]		VSC		Result: 9/29 samples (dye based) clustered in 8 groups. The other (pigment based) could not be analysed. Conclusion: TLC higher DP than other techniques.	[39]
Std dye (2) Ballpoint pen (4 red)	SE (MeOH) Sonication Centrif.	- [dyes]		Fluorescence		Result: 2 pens contained the same 4 compounds. BV10 and BR1 present in some samples. Conclusion: characterization of samples is possible.	[41]
Pens (53 black, 31 blue, 14 red, 2 green)	SE (Pyr) (MeOH:H$_2$O)	- [dyes]		VSC	Matching inks with the US international ink library	Results: pigment based (15/100) could not be analysed. Clustering in 44 groups. 82/85 inks identified in the library. Conclusion: databases are useful.	[42]
Liquid and gel pens (11 blue) (15 black)	SE (MeOH)	- [dyes]		VSC	Compare Raman to traditional TLC	Results: TLC results useful for inks soluble in solvent and not pigments. 87 % DP. Conclusion: Raman spectra is a complementary technique if TLC cannot resolve the problem.	[43]
Ballpoint pen (19 blue)(9 black)	SE (Pyr)	- [dyes]		UV-VIS Fluorescence	Differentiation, Technique comparison	Result: 82% DP (blue inks) and 92 % DP (black inks). Conclusion: destructive, no spectral information.	[44]
Ballpoint pen (41 blue)	SE (MeOH)	- [dyes]		Imaging	Potential of Imaging	Result: method optimization. Matlab to treat images. 59/820 pairs unresolved. Conclusion: 92.8% DP. Similarity> 94.5% implies that samples are the same.	[45]
Ballpoint pen (21 Black)(12 Blue)	SE (EtOH)	- [dyes]		-	Differentiation, Technique comparison	Result: 67-100% DP for black and 90-100% DP for blue pens. Conclusion: 98-100% DP with all techniques	[46]
Ballpoint pen (31 blue)	SE (MeOH)	BV1 [dyes]				Result. BV1 standard added for estimation of relative amount. 92.4 % DP, 428/464 pairs distinguished. Conclusion: MS higher DP than HPTLC, but complementary.	[47]
Ballpoint pen (13 blue)	SE (EtOH:H$_2$O 1:1)	AR18, BB26, SO3 [dyes]	HPTLC	Camag scanner III	Quality process through a new system	Results: position, color and intensity of spots digitally saved. Characterization through wavelength, distance of each spot, and intensity absorbed. Reproducibility for different scanner measurements, plates, solvent batches and examiners. Conclusion: automatic and objective comparison of samples.	[48]
					Automatic comparison through algorithms from MatLab.		[49]
							[50]
					Application the US international ink library	Results. improvements in reproducibility confirmed Conclusion: method optimized is validated and useful for matching with inks from the library.	[51]
Std. dyes	Dilution (MeOH)	BB9, BV3, BR1, SY94, AB1,FG3 [dyes]	TLC	DESI-MS	Testing surface sampling for TLC-MS coupling	Results: stepping sampling mode (manual) allows precise positions. Scanning sampling mode (automatic) maintains optimum sampling. LOD ~ ng. DESI not totally homogeneous, but all dyes were differentiated. Lower LODs than ES-MS Conclusion: DESI presents more sensitivity and versatility than TLC/ES-MS. DESI	[52, 53, 54]
		BV10,BR1,R123, AR51, AB9, FG3, FY3 [dyes]			Advantages of TLC/DESI coupling		
Ballpoint pen (8 blue, 7 black)	SE (AcN)	- [dyes]	RP-HPLC	PDAD	Differentiation using statistical tools	Results: use of 4 wavelengths. Black pens clustered in 4 groups. Blue samples (87.5 DP) easier to differentiate than black pens. Conclusion: PCA is not 100% effective.	[55]
Ballpoint pen (8 blue)		- [dyes]	RP-HPLC	PDAD		Results: use of 4 wavelengths. 97.9% of samples differentiated. PCA and LDA complementary statistical tools. Conclusion: statistical tools more effective in HPLC than IR.	[56]
Gel pen (27 blue)	SE (TBA /AcN (1:1))	AB9 [dyes]	RP-IP-HPLC	UV	Differentiation	Results: 10mmol TBA, pH 7.0, optimized conditions. Natural ageing slower than artificial. Conclusion: useful to date samples (0.5-1year).	[12]

Fountain pen (12 black) (6 red	SE (TBABr /AcN (1:1))	-[dyes]				Results: 40mmol TBABr, pH 7.0, optimized conditions. Ink degraded linearly with time. Conclusion: useful to date samples (2-3years).	[14]
Gel pen (29 black) Rollerball pen (20)	SE (EtOH)	G, TEG PEG, TEA [resins]	GC	MS	Differentiating pigment-based gel pens	Results: 29 gel pens clustered into 19 groups. Conclusion: differences between gel ink and roller black ink.	[40]
Std. dyes Ballpoint pen(black)	SE (MeOH and Sodium Acetate)	BV1,BV3,AY36,AY42,AB9, BV10 [dyes]	CE	DAD	Differentiation of inks	Results: anionic method more effective (dyes must be soluble in the BGE). All samples distinguished through five compounds through the cationic method.	[57]
Std. Dyes (50) Ballpoint pen (10 blue)		BV3,BB26,BB7,BB11,PB15, Gu [dyes]				Conclusion: Valid for different dyes. ESI-MS as confirmatory technique.	[58]
Std. dyes Ballpoint pen (8 blue and black)	Dilution (MeOH)	BB9,BB12,BB17,BCB,BB7 [dyes]	NACE	LED-UV	Create a method compatible with MS	Results: method optimization. 6/8 samples differentiated. Discrimination based on basic dyes. Conclusion: compatible with MS, future studies needed.	[59]
Std. dyes (7) Ballpoint pen (120 black)	SE (MeOH)	BV3,BV10,BR1,BB26,BB7 [dyes]		PDA	Differentiation of inks	Results: optimization of the method (LOD: 7.1-126.5 μg/L and RSD< 3.5%). Pens clustered in 6 groups. PCA needed to distinguish within groups Conclusion: DP improves with statistical tools.	[60]
Std. dyes 41 inks	Dilution (Pyr:H$_2$O)	BV3.BB26,BB11,AO7,BV10, RB31, SB21, SB3 [dyes]	MECK	UV		Results: method optimization. Extraction solvent and time (5 min), λ$_{det}$ (570, 620 and 670 nm) Conclusion: useful technique with high DP. Sample amount is higher.	[61]
Std. dyes (3)	Dilution (H$_2$O)	BR9, AO7, FY3	CE	SERRS	Application of CE-SERRS coupling	Result: method optimization (buffer, colloids) Conclusion: robust interface, not practical for analytes with positive and negative charges	[62]

[a] hyphen indicates that the analytes were not identified.

Table 5. Studies on ink composition by spectrometric techniques (elemental information)

Sample (n)	Sample Prep.[a]	Analyte	Technique	Goal	Relevant information	Ref.
Ballpoint pen (3 blue)	Dried samples in cuvettes	S,Cu,Si Mn, Fe, Ni, Ca, Zn, P, Cu ,Cl	μXRF	Differentiation Compare techniques	Results: differentiation based on quantitative composition. DP 95%. Conclusion: XRF complements IR results.	[66]
Ballpoint pen Gel pen (80 blue/red)	Dried samples in glass plates	CuPht, AB, Cu, Zn, Fe, Br, Si, P, Cl, Cr, Mn	μRaman μXRF	Combination of XRF and Raman	Results: 70% of blue and 80% red inks differentiated; identification with a database. Conclusion: Raman and XRF are complementary	[67]
2 tagged inks	-	Cr, Co, Cu, Bi, Br, Rb, Zr, Sn, Sb, I, Gd, N, Hf, Ga, Pt, Rb, Pd, Cs, Ce	EDXRF	Tagging ink samples	Results: optimization of taggant concentration: 20-80 ppm. No degradation over time. Conclusion: non-destructive technique	[68]
2 tagged inks	Scratching and dilution in H_2O	La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	TXRF		Results: qualitative discrimination (intensity ratios). Conclusion: quasi-non-destructive technique	[69]
Ballpoint pen (22 blue) 13 Taggants	Dilution (EtOH) / Dilution (EtOH) Digestion (3:1 HNO_3:$HClO_4$)	La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	INAA / ICP-MS	Determine REEs to identify samples.	Results: correlation coefficient>0.9743. LOD: 0.001-0.03 (ICP.MS), 0.0002-0.27 (INAA) Chelants identified and quantified Conclusion: fast and accurate method	[70]
Ballpoint pen (21 blue)	-	^{7}Li, ^{23}Na, ^{24}Mg, ^{27}Al, ^{29}Si, ^{39}K, ^{42}Ca, ^{51}V, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, 66Z, ^{88}Sr, ^{90}Zr, ^{118}Sn, ^{137}Ba, ^{140}Ce, ^{182}W, ^{208}Pb, ^{238}U	LA-ICP-MS	Differentiation using statistical tools	Result: raw data treated with a two-step methodology. Target elements from the batch are assessed to discriminate. Conclusion: statistical analysis provides objective results.	[71]
Ballpoint pen and gel pen (~200)	-	**LA-ICP-MS**: ^{7}Li, ^{13}C, ^{23}Na, ^{24,25}Mg, ^{27}Al, 29Si, ^{39}K, ^{42}Ca, ^{45}Sc, ^{47,49}Ti, ^{52,53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60,62}Ni, ^{63,65}Cu, ^{64,66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{103}Rh, ^{119,120}Sn, ^{137}Ba, ^{139}La, ^{140}Ce, ^{142,143}Nd, and ^{180}Hf, and ^{206,207,208}Pb. **LIBS**: Na, Mg, Al, Si, Ca, Cr, Mn, Fe, Cu, Zn, Sr	LA-ICP-MS / LIBS	Differentiation	Results: selection of discriminant elements. 97-99% DP. Differentiation among brands, between the same brands from different manufacturing places and different batches (months) Conclusion: LIBS less expensive and complex than LA-ICP-MS. Both possess high DP	[72]
Ballpoint, gel, porous, rollerball pens (34 blue) (30 black) (21 red)	-	Cu, Cr, Li, Mn, Fe, Ni, Ba, Mo, W	LIBS	Characterization of different technologies and colors	Results: Cu present in most of the samples. Li present in black samples. Pigment-based inks masked paper signal. Qualitative DP: 83, 82 and 81% for blue, black and red samples. Conclusion: simple, rapid, and semi-destructive technique. Some samples have unique formulas. A larger database is needed	[73]
Ballpoint pen (1 blue)	Dilution (EtOH) Digestion (3:1 HNO_3:$HClO_4$)	Eu	ICP-AES	Quantification of taggants (REEs)	Result: pH and Eu concentration optimized. LOD of Eu: 100ppm. Conclusion: spectrofluorometry faster and simpler than ICP-AES. Both are destructive.	[74]
Ballpoint pen (13 blue)	-	BV3,BV1.BB26,AG Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Sc, Mo, Mg, Al, Nb	TOF-SIMS	Differentiation	Result: positive mode. Different brands are easily distinguished. Bic pens differentiated through unidentified peaks. Conclusion: effective, expensive.	[75]
Ballpoint pen (10 blue)	-	BY2, BV1, BV3, BV14, BB7, BB26, AG, Na, Mg, Al, Si, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb		Differentiation through using PCA	Result: positive mode. 10 measures/sample. 91% DP. No differences between old and new samples. Differences between batches. Conclusion: rapid, non-destructive, organic and inorganic information.	[76]

[a] Hyphen indicates no sample preparation needed for the analysis.

Table 6. Studies on ink composition by spectrometric techniques (molecular information, UV, IR and Raman).

Sample (n)	Sample prep[a]	Analyte[b] [compound]	Technique	Goal	Relevant information	Ref.
Ballpoint pen (50 blue)	Dilution (EtOH) Centrifugation	- [dyes]	UV-Vis	Differentiation with statistical tools	Result: samples clustered in 2 groups. 3 PCs. 100% DP. Conclusion: statistical algorithms useful for differentiation.	[79]
Std. dyes (2) Ballpoint pen (25 black)	Dilution (EtOH)	BV1 [dyes]		Statistical tools to create a database	Result: 3-4 PCs to characterize samples. Extractant influenced on the results. Slight variation in replicates from the same pen. Conclusion: a database can be used.	[80]
Ballpoint pen (21 Black) (12 Blue)	SE (EtOH)	[dyes]		Differentiation, Technique comparison	Result: clustering (5 black and 3 blue groups). DP: 96% in black, 79% in blue. Conclusion: 98-100% total DP.	[40]
Ballpoint pen (10 blue)	SE (EtOH)	BV1, BV3 [dyes]			Result: UV-Vis cluster in 8 groups. Lines and inks from the same pen, same spectra. Conclusions: complementary techniques, UV-Vis more DP than IR.	[32]
Ballpoint pen (19 blue) (9 black)	-	-	HSI		Result: 100% samples differentiated. Visual and spectral information. Conclusion: non-destructive, fast, more DP than TLC.	[44]
Gel pens (15 blue) (13 red) (14 black)	-	- [pigments] [dyes]	VSC (UV-IR) HSI	Differentiation Advantages of HSI	Result: 100% DP for red pens, 90 % DP for blue pens, 38% DP for black pens. Conclusion: efficient, non-destructive, need for complementary techniques, objective.	[81]
Ballpoint pen (10 blue)	SE (EtOH)	BV1, BV3 [dyes]	IR	Potential of IR-PCA in the analysis of inks	Result: IR cluster samples in 7 groups. Lines and inks from the same pen, same spectra. Conclusions: complementary techniques, UV-Vis more DP than IR.	[32]
Ballpoint pen (108 blue)		TAM [dyes] ER, AlR [resins]	FTIR	Patter recognition technology to identify inks	Result: clustering in two groups (inks with or without C=O bond). Inks with C=O bond clustered in 6 subgroup. Inks without C=O bond clustered in 29 subgroups. Conclusion: fast, reliable, non-destructive.	[31]
Ballpoint pen (12 blue) (21 black)	Dilution (EtOH) Evaporation	TAM		Differentiation	Result: detection of non-colorant components. TAM appeared in most of the samples. DP: 80%-82% (black groups), 95% (group 1 blue). Conclusion: 98-100% total DP.	[46]
Ballpoint pen (27 blue) (23 black) Gel pen (10 blue) (9 black)	Dried sample on glass plate	BV1, AB, ABl, PB15:2, SB38 BA, S, EG, G [dyes, pigments]	μ-FTIR	Characterize inks Technique comparison	Result: 95% of ballpoint and 90% of gel pens distinguished. More discrimination power when μ-XRF used. Conclusion: IR and XRF complementary.	[66]
Inks (2 black)(1 red)	-	C-H group (AH) OH group	SR-FTIR	Advantages of SR-FTIR	Result: overlapping of spectra. High resolution and sensitivity (200 times better than FTIR). Paper can interfere. Conclusion: rapid identification of inks.	[82]
Ballpoint pen (8 blue)	-	-	μ-ATR-FTIR	Differentiation using statistical tools	Result: overlapping, paper interferences. 62.5% of samples differentiated. PCA and LDA complementary statistical tools. Conclusion: statistical tools more effective in HPLC than IR.	[56]
Ballpoint, roller bal and gel pen (100 blue)	-	-	ATR-IR	Potential of statistics in the analysis of inks	Result: 100% correct classification by brand using LDA-SPA and LDA-GA models. Conclusion: faster and objective results.	[83]
Gel ink (55 blue)	-	PB15, PV23 [pigments]	Raman	Potential of Raman for ink analysis	Results: 36/55 samples were pigment-based. Clustering in 5 groups using 2 lasers. Total DP of 68%. Conclusion: the database created is useful	[84]

Ballpoint pen (26 blue, 26 black) Fluid ink (63 blue, 60 black, 36 green, 48 red)	Addition of ply-l lysine and Ag colloid (SERRS)	-[pigments]	Raman, SERRS		Results: SERRS show a DP between 28.2 and 92.7 % depending on the sample type. Conclusion: useful to complement other techniques. Depending on factors, results are different. Using this technique alone is not recommendable.	[85]
Ballpoint pen (blue, black) Fluid ink (blue, black, green, reed)	Addition of ply-l lysine and Ag colloid (SERRS)	-[pigments]	SERRS	Potential of SERRS compared to Raman	Results: DP ranged between 34.6-96 % depending on the sample and technique. Conclusion: SERRS enhance the DP	[86]
Documents (2) Pen (10)	Dropping of Au colloid on the surface	-	SERRS	Potential of gold nanoparticles	Results: original and copied documents are distinguished. Pens are also differentiated. Conclusion: Au nanoparticles are stable enough. Promising results.	[87]
Liquid and gel ink (11 blue) (15 black)	Dropping Ag colloid		Raman, SERRS	Compare technique performances	Results: Raman, 56 and 77 % DP for blue and black samples. SERRS, 71 and 90%, respectively. Conclusion: Complementary techniques, more effective than VSC. Complementary to TLC.	[88]

[a] Hyphen indicates that no sample preparation was necessary for the analysis

[b] Hyphen indicates that analytes were not identified

Table 7. Studies on ink composition by spectrometric techniques (molecular information, analytical MS).

Sample (n)	Analyte [compound]	Technique	Goal	Relevant information	Ref.
Ballpoint pen (44 blue) (23 black) (10 red)	BR1, BV10, BV3, BV1, SB23, BB26, SB2, BB7, SO3, AY36, AB92, AB9, SB38, SBr20, SB7, SY47, SY49, SY19, AG, CI, A [dyes]	ESI-MS	Automatic dye identification using a database	Results: A major peak for each dye detected. MS/MS required in some samples (BV10, BR1). SY19 did not provide any peak. Fluorescent light degraded samples. Conclusion: useful database created with 77 samples.	[94]
Ballpoint pen (6), Rollerball pen (6), Gel pen (6) (all black)	BV1, BV3, AY36, BTA, DEG, DEP, ED, EG, PVP, G, PE [carriers, dyes, pigments]		Differentiation	Results: pigments in gel inks. BV1, AY36 and PE in BP. BTA and TEA in gel and rollerball pens. Unidentified peaks to distinguish. Solvent peaks disappear with time. Conclusion: quasi-non-destructive, multiple information about carriers, dyes and pigments.	[95]
Std dye (2) Ballpoint pen (4 red)	BV10, BR1 [dyes]		Differentiation through TLC spots	Result: ESI-LC-MS identify analytes, soft ionization, clear spectra. Conclusion: confirmatory technique.	[41]
Ballpoint pen (2 red) Std. Dyes Sample from 1967	BV10, BR1, R123, BV2, BV3 [pigments]		Characterize trough degradation mechanisms	Result: BV10 and BR1 degraded in different products with photodegradation. BV3 degraded similarly to BR1 and BV10. R123 and BV2 different and unknown mechanism. Conclusion: LD-MS not enough. Photodegradation helps for differentiation. Differentiation in samples from the same batch.	[96]
Gel pen (207) (8 colors)	PB17, PG 36, PO13, PV23, PR12, PBk7, PEG [pigments]		Characterize through pigments	Result: orange (PO 13, defragmentation mechanism via 4 paths); pink (PR12 + two dyes); black (based on carbon, difficult analysis). PEG may be used to date. Conclusion: good characterization as pigments do not degrade.	[97]
Std. dyes Ballpoint pen (33 blue)	SB38, PB15, AB9, AB92 [dyes, pigments]	LDI-TOF-MS	Differentiation	Results: negative mode. 87.9% DP. Increased to 96 with relative peak areas. Increased to 99.6% with unknown peaks. Conclusion: high DP, quasi non-destructive, optimization required.	[98]
Gel Pen (33)	BV3, BV4, SB38, PB15, PV23 [dyes, pigments]		Statistics to create an objective method	Results. 92% DP in negative mode, 77% in positive mode. Conclusion: statistics higher DP than comparison of relative areas. Pearson Correlation better than Euclidean.	[99]
Ballpoint pen (23 blue) (15 black) (12 red)	BV1, BV4, BB26, VB7, PB17, BR1, BV10 [dyes]		Differentiation	Results: no differences between solid inks and inks on paper. Clustering in 10 blue, 5 black and 3 red groups. Conclusion: applicable to real cases.	[100]
Dyes Ballpoint and liquid pen (Blue, red)	BV3, AY36, AB49, AB90, FY3, AR7, AR92 [dyes]		Detection of multiply-charged dyes	Results: only MALDI-TOF-MS can detect polionic dyes (AB49 and AB90). Conclusion: neutral, anionic, cationic, polyconic solvents and pigments can be analyzed and used for identification. TLC can support results.	[101]
Std dye (2) Ballpoint pen (4 red)	BV10, BR1 [dyes]	MALDI-TOF-MS	Differentiation through TLC spots	Result: identification of BV10 (2 samples) and BR1 (2 samples). Conclusion: complementary with ESI-MS and TLC	[41]
Ballpoint pen (31 blue)	BV3, BB26, BB7, BB2, BV4 [dyes]		Differentiation Techniques comparison	Result: 48% of peaks unidentified. 99% DP. 460/465 pairs distinguished. Ageing modifies results. Conclusion: LDI more effective than HPTLC.	[27]
Gel pens (40 black) (5 blue)	BB7, BV10 (blue) BB26 (black) [dyes] POE, PEG [surfactants]		Differentiation	Result: HPLC-QTOF-MS and TLC only to for confirmation. 15 samples without surfactants. 100% differentiation. Conclusion: effective and non-destructive technique.	[30]
Ballpoint pen (2 black) Banknotes, checks	BV3 [dyes]	SALDI-IMS	Differentiation through molecular imaging	Result: gold nanoparticles deposited directly on the sample. Thickness influenced on the measurement but improve the detection due to their conductivity. Conclusion: applicability to caseworks/other samples demonstrated.	[102]
Ballpoint pen (13 blue)	BV3, BV1.BB26, AG [dyes]	TOF-SIMS	Differentiation	Result: positive mode. Different brands are easily distinguished. Bic pens differentiated through unidentified peaks. Conclusion: effective, not for routine analysis.	[103]

Ballpoint pen (10 blue)	BY2, BV1, BV3, BV14, BB7, BB26, AG [dyes]		Differentiation through using PCA	Result: positive mode. 10 measures/sample. 91% DP No differences between old and new samples and between batches. Conclusion: non-destructive, organic / inorganic information.	[76]
Ballpoint pen (13 black) (10 blue) Fluid ink (10 black) Gel pen (10black)	G, DEA, TEA,BV3,PAl,TG, PE,DP [dyes, carriers, resins]	DART-MS	Differentiation	Results: only protonated species analyzed. 2 samples undistinguishable. Spectra depended on the analysis position, spectral library created. Conclusion: rapid and non-destructive method.	[104]
2 inks	BR1, BB7 [dyes]	DESI-MS	Capabilities and application of imaging MS	Results: sample ionized in ambient conditions. The DESI method is automatic and save images in 2 dimensions. Images are the spatial distribution of the ions. Conclusion: inks successfully differentiated. Valid for biological samples.	[105]
Ballpoint pen (10 blue) A forged text Old document (1981)	AG, BV3, BB26, BB7, SB2 [dyes]			Results: optimization of the method (flow).. No paper interferences (except inkjet paper). Spray influences on the results. Degradation products of BV3 on the old document. Imaging can be optimized. Conclusion: Successful dye identification. Quasi non-destructive, applicable to real cases	[106]
Ballpoint pen (red, blue) Real case	BV3. BB26, BB7, NP, DDG (blue). BV10, BR1 (red) [dyes]	EASI-MS	Fingerprinting of inks samples	Result: BV3 was identified in all the blue ballpoint pens. Two inks detected in the same symbol (real case). Conclusion: fast, non-destructive, superficial information.	[29]

Table 8. Studies on printer inks

Sample (n)	Sample Prep.[a]	Analyte[b] [compound]	Technique-Detector		Goal	Relevant information	Ref.
Colour inkjet cartridge (23)	SE (Pyr/H_2O (4:3), reconstituted EtOH/H_2O (1:1)	-	TLC	UV	Database to identify cartridges	Result: samples clustered in 18 groups. Discrimination <100%. Magenta presents more compounds than cyan and yellow. Conclusion: not 100% effective method	[112]
			HPLC	PDAD			
[103]Toner (8 black)(3 color)	-	*AB,* UCH, furans, phenols [other]	La-Py-GC	MS	Differentiation	Results: 100% differentiation, low reproducibility. Direct analysis. No paper interferences. Conclusion: micro destructive, more studies needed	[113]
Toner (93 black)	Soldering iron Pyrolysis	-	Py-GC	MS	Differentiation using statistics	Results: PCA clustered samples through 8 peaks. Conclusion: statistics are needed for objective interpretation	[114]
Colour inkjet cartridge (22)	SE (BGE), Sonication, Centrifugation	-[dyes]	MECC	DAD	Optimize a CE method	Result: repeatability (RSD < 3.3%) Reproducibility (RSD<3.3%). Different wavelengths for differentiating similar samples. Conclusion: a more discrimination needed	[109]
Colour inkjet cartridge (37)					Application of the method	Results: cartridges with the same ink not distinguished.	[115]
Inkjet inks (18)	Dilution (DMSO) sonication centrifugation				CE method for characterization of inks	Results: reproducibility low RSD. HP inks different from the remaining brands. Similar method for colour/black inks. good precision Conclusion: a wider set must be analysed	[116]
Blue, cyand and magenta pure colors (3)	SE (optimization)	-	-	UV	Optimize the best extractant	Results: Best extractants are a) 40 mM borate buffer with 20 mM SDS and 10% CAN; b) 80 mM borate buffer with 50 mM SDS and 10% MeOH. Conclusion: these extractants are relevant if CE is carried out to analyse samples.	[117]
Inkjet inks (13 black)	SE (DMSO MeOH, Pyr:H_2O 1:1 or AcN:H_2O 1:3)	BV1, PB15, BV10, BB11, BB26	CE	ESI-TOF-MS	Study the potential of CE-MS	Results: DMSO selected as the best extractant. CE-MS parameters optimized for the method. Precision (RSD) calculated between 0.04-11.45%. Conclusion: CE can qualitatively differentiate among samples. Coupling to MS increases the DP.	[118]
Offset ink (1)	Addition of REE's (chelates)	La, Pr, Nd, Sm, Eu, Gd [REE's]	PIXE		Differentiation using tagging	Results: no quantification. LODs not calculated. Conclusion: samples 100% distinguished	[119]
Toner (4)	-	Ti, Sr, V, Ti, Cu, Fe [elements]	EDXRF		Combination of XRF and PLEAF	Results: XRF can differentiate if letter fonts are larger than 20. Not valid to estimate the sequence of intersections. Conclusion: PLEAF as secondary technique for confirmation, more sensitive.	[120]
Toner (162	-	Fe, S, Cr			Classificati	Results: 28 groups with ED-XRF. 14	[121]

black)		S, Ac, MMA,TiO$_2$ [pigments, polymers]	MK-FTIR	on of toners	groups with MK-FTIR. Fe and S prominent elements. Conclusion: differentiation of models. Combination of techniques provides more DP	
Toner (807 black)	Soldering iron	SCA, PEt, SiO$_2$, PB27 [polymers, pigments]	R-A IR	IR spectra library	Results: clustering in 98 groups. Identification of manufacturer. SCA present in 75% samples Conclusion: efficient spectral library. Applicable to real cases	[122]
Toner (430 black)				Discrimination	Results: 95.81% of samples classified with PCA Conclusion: efficient for toner differentiation.	[123]
Toner (108 black)	Soldering iron	Bisphenol A, resins, TiO$_2$ [polymers, additives]		Differentiation using statistics	Results: clustering in 15 groups. Manufacturers identified Conclusion: low cost, fast, quality results. This study is similar to [114]	[124]
Toner (54 black)	-	SCA	IR		Results: printer and photocopy samples. 95% of pairs distinguished. Conclusion: more studies are needed. Study similar [114]	[125]
Toner (138 black)	Scratching with a scalpel	esters, OH, MA [polymers, resins]	FTIR	Spectral library using a diamond cell	Results: database created. Optimization of the method Precision repeatability RSD <0.13%, intermediate <0.4%. Samples contain more than 80% polymers Conclusion: effective method, useful database	[126]
Toner (201 black) (23 color)	-	Al,Cr,Hg,Si,Sr,U,Bi, Cu,Mn,Pb,Ta,Th,Ti, V,W,Zn PB15, PR15, PB122, PY12 [pigments]	LA-ICP-TOF-MS	Differentiation using statistics	Results: photocopy/printer toners analyzed. Different pigments detected. Strongest signals are subjected to CA and PCA analysis Conclusion: statistics are useful tools. Cu as cyan marker for cartridge differentiation	[127]
Inkjet (25) Toner (27) (black)		LA-ICP-MS: Mg, K, Cu, Ni, Zr, Li (inkjet); Pb, Ti, Zn, Ce, V, Ba, La, Mg, Co, Al, Fe, Mn, Si, Sr, Cu, Zr, Ni, Cr (toner). LIBS: Mg, K, Cu, Li (inkjet); Mg, Sr, Zn, Mn, Fe, Ni, Sc, Al, I, Zr, Cu, Ti, Sb, Co, V, Y, Rb, S, K, Na (toner)	LA-ICP-MS LIBS	Characterize toners/inkjets	Results: different methods depending on the sample type. Paper interferes in the results. Samples are homogenous. Discrimination between 88-100%. More DP than other techniques such as SEM-EDS. Conclusion: methods are valid when effective standardization is made. Analysis of writing inks might be performed to show the potential of the method.	[128]
Inkjet Cartridge (color) (black)	-	PBk7, Surfynol, PB15, PV19,PR122,PY74 [Pigments, polymers]	LDI-TOF-MS	Identification of pigments	Results: complete characterization of the colors and black inks. Anionic mode more effective. Overlapping.	[129]
Inkjet ink (2)	-	BV1,OA,SBl, TEG [dyes, solvents, other]	FAB-MS	Test LDI-TOF-MS and FAB-MS.	Results: LDMS positive mode to detect dyes. FAB detects all compounds. More expensive than traditional methods. The two samples are differentiated.	[25]
Inkjet cartridge	-(Matrix)	PEG	LD-MS, MALDI-MS	Combination of MS	Results: Raman not valid for black samples. In-house software for black	[130]

(10 black and color)			and Raman		samples differentiation by LD-MS. Cyan cartridges difficult to distinguish. Conclusion: MALDI and raman for colored inks. LD-MS for black inks	
Inkjet (217) (black, colour)	SE (EtOH)	-	DART-MS	Classify inkjets	Results: black samples from different manufacturers differentiated. Coloured samples identified by MS combinations. Conclusion: high sensitive technique.	[131]
Inkjet (25) Toner (27) (black)		Mg, Cu, K, Al, Mn, Fe, Pb, Si	SEM-EDS	Differentiation using statistics	Results: DP of 70.7 % Conclusion: can be used as complementary technique	[128]
Toner (166 black)	Removing ink of paper (cuts)	Al,Si,S,Cl,C,Ti, CrMn,Fe,Zn [elements]	SEM-EDX	Characterize toners/inkjets	Results: clustering in 13 groups. 41% of samples assigned to brands. Conclusion: statistics needed for objective interpretation. Hager DP combining two techniques.	[114]

[a] Hyphen indicates that no sample preparation was necessary for the analysis

[b] Hyphen indicates that analytes were not identified

Figure 1

a)

Ballpoint pen
Gel and rollerball pen
Fountain pen
Unknown

Dating (28%)   Differentiation (72%)

20%
5%
14%
61%

Other 8%
Intersections 8%
Paper 7%
Printer 15%
Pen 62%

b)

Other spectrometric techniques
Analytical MS

45%   55%

% Articles

2000-2002
2003-2005
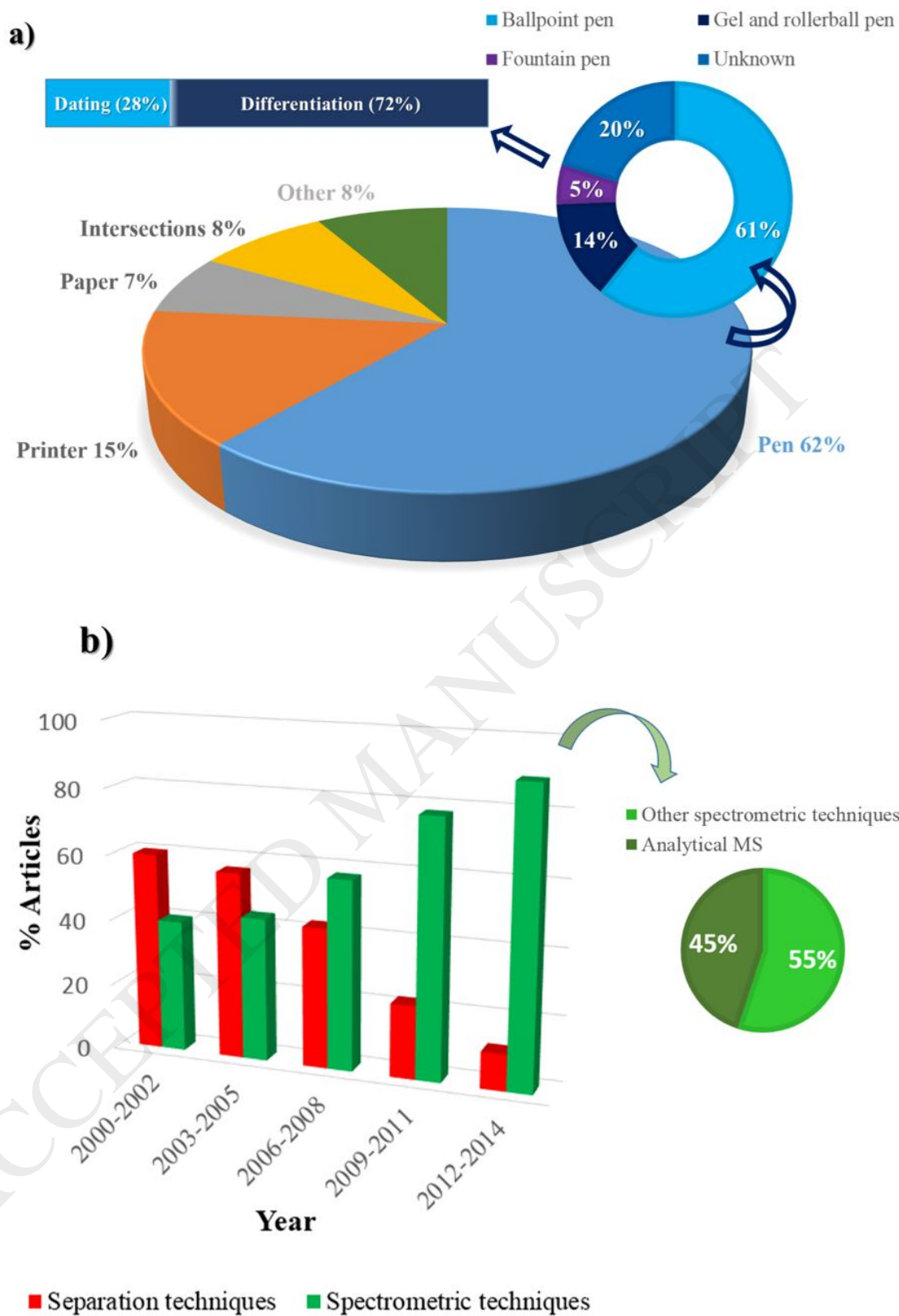2006-2008
2009-2011
2012-2014
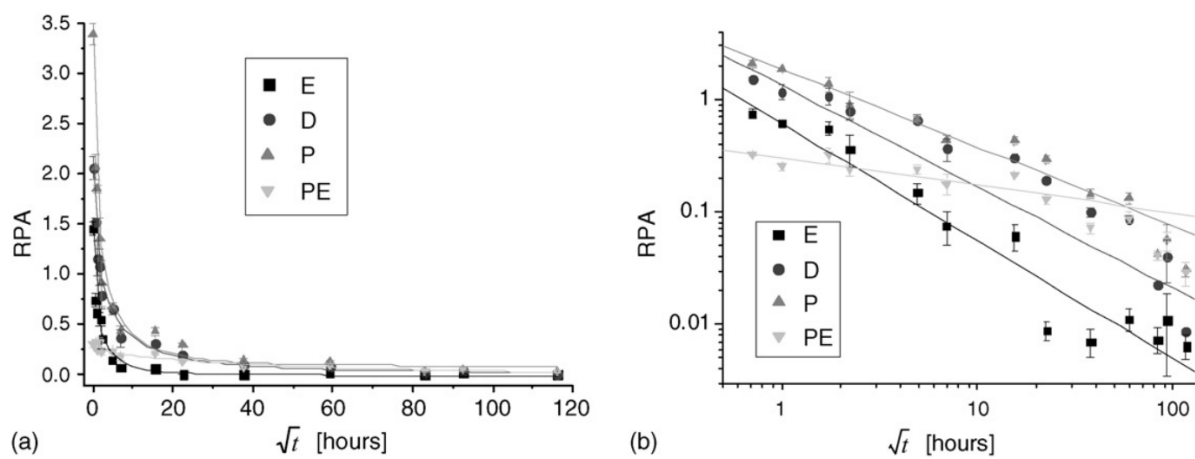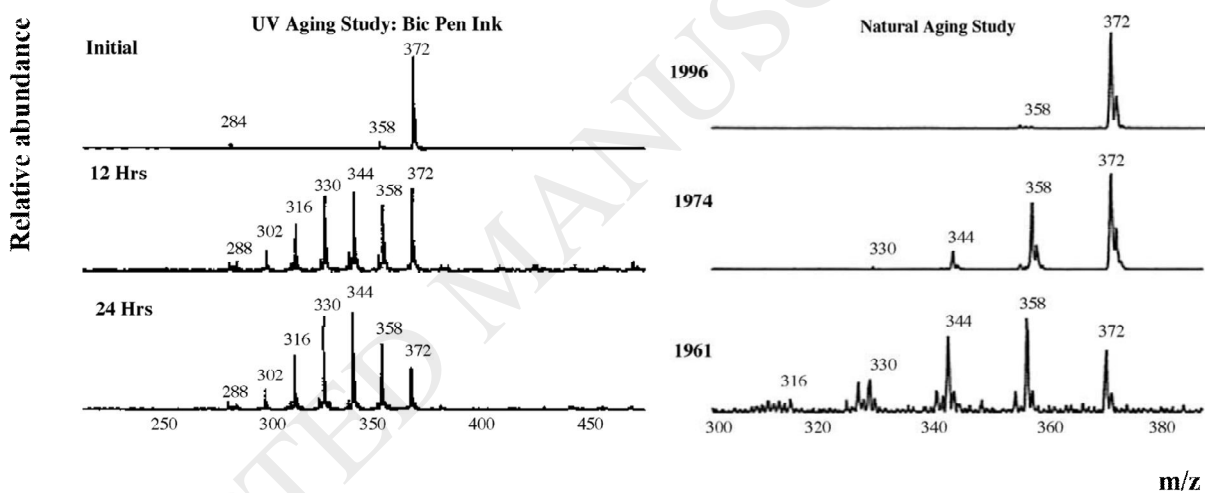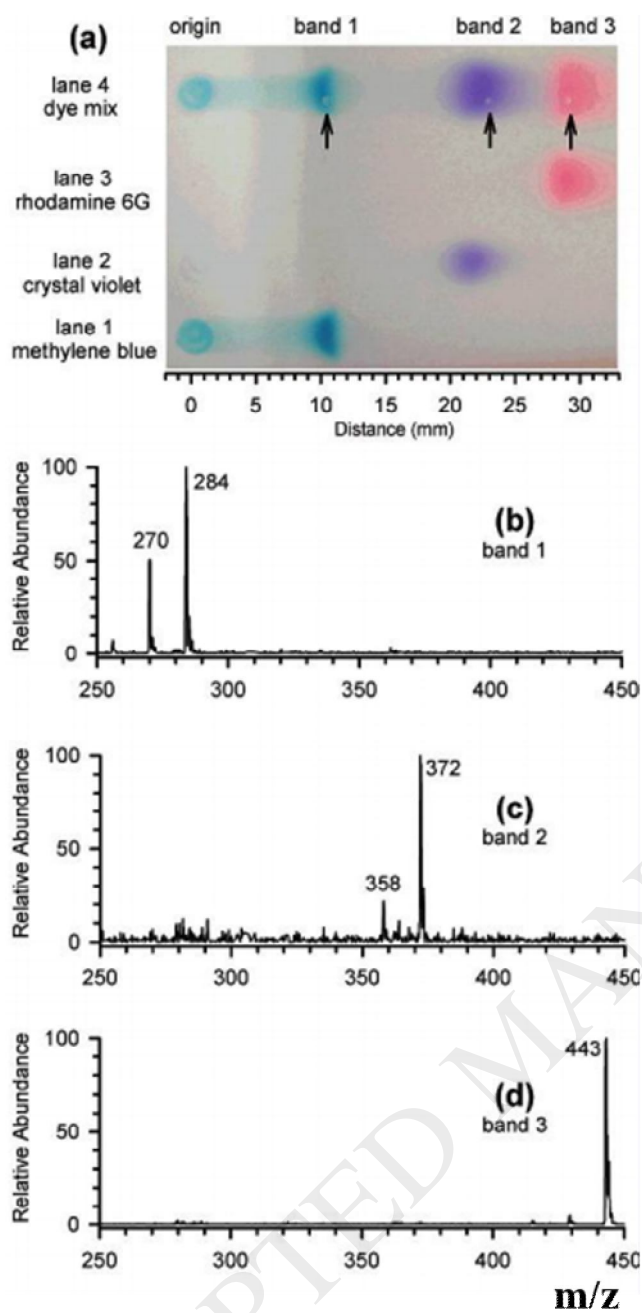
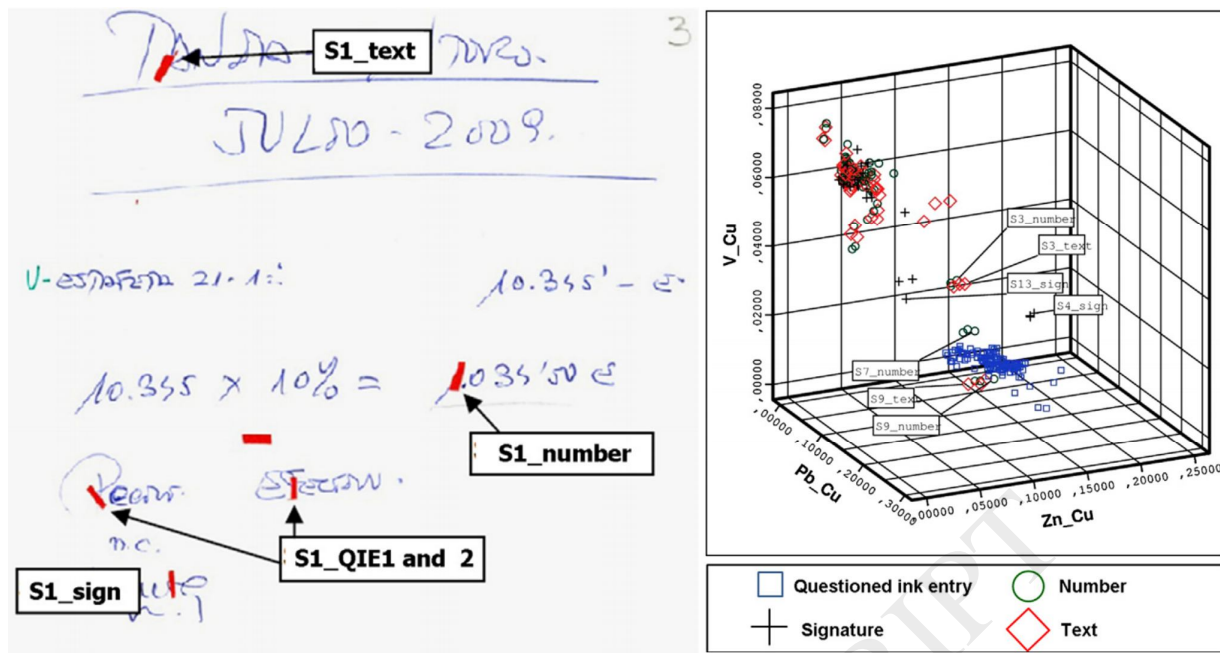Year

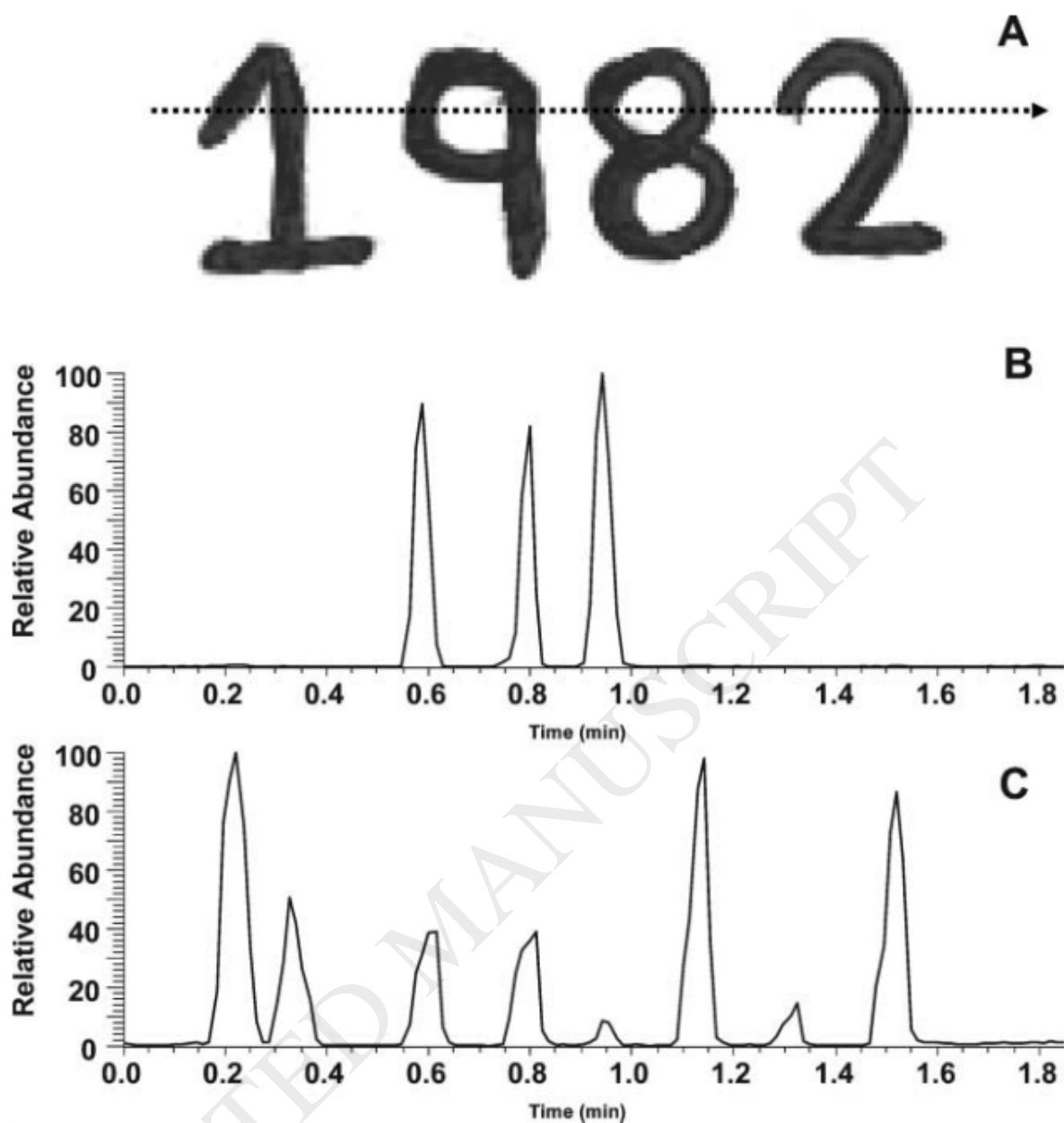Separation techniques   Spectrometric techniques

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7