

*Technical paper*

# Extraction of Colour Inkjet Printing Inks from Printouts for Forensic Purpose

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## Abstract

The ability to differentiate between inkjet printing inks is of great interest in document examination. The aim of this work was to develop a procedure for effective ink extraction so that the ink could be reliably analyzed by capillary electrophoresis. Conditions such as type and composition of extracting mixtures, as well as duration of extraction and sonication procedures were taken into consideration. A set of different agents was used to extract inks of inkjet printers produced by Hewlett-Packard, Canon, Brother, Epson and Lexmark. Extraction efficiency was examined visually and then by means of UV/Vis spectrometry. It was ascertained that the most promising extracting agents are mixtures of borate buffer with SDS and with acetonitrile, or alternatively with methanol, which are both suitable background electrolytes for further CE analysis. However, in some exceptional cases, highly efficient extraction was achieved by a mixture of DMF, DMSO, EtOH and MEE with water.

**Keywords:** Extraction, inkjet printing inks, UV/Vis spectrophotometry, forensic investigations

## 1. Introduction

Documents that have been printed by inkjet printers are increasingly frequently being submitted for forensic examination. With the advent of this technology, use of inkjet printers to commit crimes such as counterfeiting has become very widespread among criminals. The crime of forgery generally concerns the making of fake documents (certificates or identification cards), false banknotes, stamps and checks, the changing of an existing document (e.g. prescription) or the creation of a signature without authorization (false stamps, false signs). In connection with this, the detection of alterations or additions to a document and the determination of the time when the document was printed are the prime concerns of document examiners. Verification and authentication of printed documents solely on the basis of the inks that have been used is a major problem. Moreover, even the first step of instrumental analysis – extraction – can be very difficult.

Printing ink consists of three major components – a colouring matter, a solvent, a binder and various additives

such as dryers, dispersants or UV-blockers.<sup>1,2</sup> The colouring matter – a colourant – is either a dye or a pigment. Dyes differ from pigments in that they are soluble in the vehicle, are transparent and create relatively small drops and have low resistance to externals.<sup>3</sup> It should be noted that many dyes are composed of several substances and derivatives that are chemically very similar and often hard to distinguish. Furthermore, modern demands for specialized printing instruments have resulted in an explosion of ink formulations; each of these may contain dozens of sophisticated additives.<sup>4</sup> This wide array of other ingredients typically forms a small fraction of the overall ink composition.<sup>5</sup> Such a variety of ink components may create some analytical difficulties, but – on the other hand – it makes it easier for forensic examiners to differentiate inks by the use of different analytical methods. There are many techniques which have been used in such cases, although their partial destructive character: capillary electrophoresis (CE),<sup>4, 6–13</sup> thin layer chromatography (TLC),<sup>5, 14–22</sup> high performance liquid chromatography (HPLC),<sup>22–28</sup> spectrophotometry UV-Vis,<sup>14, 15, 29</sup> Fourier transform in-

frared spectroscopy (FTIR)<sup>14</sup> and mass spectrometry (MS).<sup>30, 31</sup>

One should be aware that the existence of various printing ink formulations can lead to a serious problem with selection of the most efficient extracting agent for colouring matter.<sup>7</sup> When choosing an extracting agent, the forensic examiner should take into account the composition, polarity, density and viscosity of selected reagents. Boiling point, resistance and purity of solvents as well as the disadvantageous influence of the extracting mixture on analyzed inks (oxidation, disintegration) and paper (physical damage) are also very important factors.

Organic solvents in which such kinds of undesired self-activating processes occur should be categorically rejected. All the mentioned features can have a serious impact on the sample preparation process and subsequent analysis. In Table 1, the extraction procedures that are recommended in the literature for using together with above-mentioned separation methods for analysis of not only inkjet printing inks but also other kinds of inks are listed.

A literature search reveals that there is a lack of a procedure that is specific for extraction of inkjet inks from paper before CE analysis. The aim of this study was to de-

**Table 1:** The extraction methods used for the extraction of various kinds of inks.

Material/ink from	Extracting agent	Duration of the influence of (min) solvent	sonication	Further analytical method	Ref.	
Ballpoint pens	<b>Acetonitrile (ACN) : electrophoretic buffer (1:1, v/v)</b>	–	<b>10</b>	<b>CE</b>	<b>7*</b>	
	<b>Dimethylformamide (DMF)</b>	–	<b>5</b>	<b>CE</b>	<b>4</b>	
	<b>Methoxyethoxyethanol (MEE)</b>	–	<b>5</b>			
	<b>Methanol (MeOH)</b>	–	<b>2÷5</b>	<b>CE</b>	<b>8, 9</b>	
	<b>Pyridine : water (1:1, v/v)</b>	–	<b>5÷15</b>	<b>CE</b>	<b>6</b>	
	ACN (80%)		2	HPLC	23	
	Benzyl alcohol	30	–	ESI/MS	30	
	Ethanol (EtOH)	lack of data	lack of data	UV-Vis, FTIR, TLC	14	
		lack of data	lack of data	UV-Vis, TLC	15	
	EtOH : water (1:1, v/v)	15 (100 °C)	–	HPTLC	16	
	MeOH	1	–	TLC	17	
	Fountain pens	<b>EtOH : water (1:1, v/v)</b>	–	<b>15</b>	<b>CE</b>	<b>10</b>
<b>MeOH : borate buffer (5mM) (1:1, v/v)</b>		–	<b>15</b>	<b>CE</b>	<b>11</b>	
Benzyl alcohol		10	–	TLC	18	
Tetrabutylammonium bromide buffer (40mM) : ACN(1:1, v/v)		720	–	HPLC	26	
Rollerball pens		<b>Ammonia (28%)</b>	–	<b>5÷10</b>	<b>CE</b>	<b>12</b>
Fiber tip pens		<b>Oxalium (0.5%)</b>	<b>15</b>	–	<b>CE</b>	<b>13</b>
Gel pens		DMF	20	–	UV-Vis	29
		Dimethyl sulphoxide (DMSO)	lack of data	lack of data	TLC	19
		EtOH : water (1:1, v/v)	0.5	–	TLC	5
		Tetrabutylammonium bromide buffer (40mM) : acetonitrile (1:1, v/v)	720	–	HPLC	27
		Inkjet printers	<b>MEE</b>		<b>5</b>	<b>CE</b>
		Dichloromethane	a few	–		
	HCl : MeOH (35:65, v/v)	–	–	HPLC	28	
	Pyridine (80 °C)	5 (80 °C)	–			
	DMF	1	–	TLC	20	
	Sulphuric acid(VI)	1	–			
	Pyridine : acetic acid (3:1, v/v)	lack of data	lack of data	TLC	21	
	Pyridine: water (4:3, v/v)	30	–	TLC, HPLC	22	

\* Procedures of extraction intended to CE are printed in bold.

velop such a procedure. Furthermore, taking into account the forensic purposes which such analyses would serve, it was required that the procedure should be efficient enough to allow not only the ink components to be well identified by means of CE but, in addition, that inks of different brands should be well distinguished. The extractant was also expected to have such physicochemical properties as would enable the sample preparation procedure to be as simple and fast as possible.

## 2. Experimental

### 2.1. Chemicals

The chemicals used for preparing the extractants were: Brij-35, methoxyethoxyethanol (MEE), sodium dodecyl sulphate(IV) (SDS) – all produced by Sigma-Aldrich (Steinheim, Germany); acetonitrile (ACN), dichloromethane, dimethyl sulphoxide (DMSO), ethanol (EtOH), formic acid, hydrochloric acid (32%), methanol (MeOH) – produced by Merck (Darmstadt, Germany); ammonia (28%), dimethylformamide (DMF), isopropanol, pyridine, sulphuric acid(VI) (95%), acetic acid – produced by POCH (Gliwice, Poland). All the organic solvents were of HPLC grade or p.a. purity.

### 2.2. Apparatus

The extraction process was carried out in a Sonic 3 ultrasonic bath (Polsonic, Poland). A UV-Vis Lambda 25 spectrophotometer (PerkinElmer, USA) was used to measure the efficiency of extraction of inks from paper. Spectra were processed by original operation system UV WinLab. Each spectrum was acquired in the region of 250–800 nm and rationed against a reference spectrum of background (blank sample). An MPW-250 centrifuge (MPW Med. Instruments, Poland) was used to centrifuge the samples before spectrophotometric measurements.

### 2.3. Extraction of Pure Inks

26 different extractants, presented in Table 2, were prepared for preliminary examination. Most of them were selected on the basis of the literature presented in Table 1. Two mixtures, i.e. borate buffer with SDS and acetonitrile as well as borate buffer with SDS and methanol, were additionally tested because they can serve as background electrolytes in CE analysis. Another innovative idea was to use each of the following organic solvents: DMF, DMSO and MEE with water (instead of alone) as the extraction efficiency was observed to increase, in general, in the presence of water.

In order to pre-select the optimal extracting agent the most prevalent among computers owners producer of inks was chosen. Therefore, pure inks of three colours:

Yellow (C4838A), Magenta (C4837A) and Cyan (C4836A) taken from the Business Inkjet 1200 printer (Hewlett-Packard) were extracted from paper using all the above extractants. Printouts were prepared using ordinary and commonly available printing paper – PolSpeed (International Paper, Poland) of 80 gm<sup>-2</sup> basis weight. Two circular pieces (i.d. = 0.4 cm) of paper printed with ink of a given colour (Yellow, Magenta or Cyan) were punched out and transferred to a vial. Ink was extracted by adding an extracting agent (2 mL). The vials were capped to prevent evaporation and left for 30 minutes to extract. A blank sample was obtained by punching out 2 chads of blank paper (of the same size as the test samples) near the ink sampling location. They were subjected to the extraction process in the same conditions as all the test samples.

The extraction efficiency was evaluated visually using a 5 degree scale from 0 (no extraction) to 100% (all the ink was extracted, the remaining paper was white). The first observation was made after 30 min. of the extraction process and then samples were put into an ultrasonic bath where total extraction of ink could be carried out. The effects achieved during this step were monitored after 5 and 15 minutes (Table 2).

After the completed extraction procedure (30 + 15 min.), 13 selected extracts (Table 3) were centrifuged and the intensities of their hue were measured by the UV/Vis spectrophotometer. In each case, the analytical signals were integrated in relation to the baseline taking either single or double-peak bands into account. Because of the fact that from the forensic point of view extraction of every colour dye (Yellow, Magenta, Cyan) is equally important, the arithmetic mean of the signals obtained for these dyes was considered as a general estimation of the extraction efficiency.

### 2.4. Extraction of Mixed Inks

To verify the usefulness of selected reagents in the extraction of real samples, printouts of mixed inks created with the use of different inkjet printers were examined. The samples were taken from 15 different models of printers produced by Hewlett-Packard, Canon, Brother, Epson, and Lexmark (see Table 4). Each printer was equipped with its own dedicated ink cartridge (except Pixma MP210 and Pixma iP1800 printers, which were operated with the use of the same cartridges).

Using each of the mentioned printers, four squares (each of 0.9 × 1.2 cm) were printed in rainbow-style on PolSpeed paper and then cut out and extracted by adding each of the four selected extracting agents (1 mL). The vial was closed to avoid evaporation and put into the sonication bath for 15 minutes. After that, the extract obtained was centrifuged. Then, the extraction efficiency was measured spectrophotometrically and interpreted as described previously.

### 3. Results and Discussion

#### 3. 1. Efficiency of Pure Inks Extraction

It can be seen from the results presented in Table 2 that, in general, inks of different colours are affected differently by particular extractants.

Most likely, this is caused by a difference of chemical structure of dyes and their affinity to the applied solution. By comparing results obtained at different stages of extraction, the positive impact of sonication on the effectiveness of extraction is observed. 5 min. in the ultrasonic bath induced significant changes in the hues of the solutions – the extraction degree of each of the examined inks was equal to or greater than 50% after using 8 extractants. After the next 10 min. (15 min. altogether) of sonication, the number of such reagents increased to 13, including both CE buffers and DMF, DMSO and MEE solutions mixed with water.

In order to obtain more objective and accurate results, the extraction efficiency was then evaluated by means of UV/Vis spectrophotometry. To this end, the 13 extracting agents pre-selected above were used and, in addition, it was decided to test a mixture of DMF,

DMSO, EtOH and MEE with water as an extracting agent.

Spectra of Yellow and Magenta inks were characterized by single intensive bands situated from 300 to 520 nm and from 450 to 610 nm, respectively. The Cyan extracts gave spectra with two distinctive but not totally separated bands in the spectral region typical for blue dyes, i.e. between 500 and 775 nm (presumably displacement of band maxima was a consequence of interaction of dyes with the extracting reagents used). In Figure 1, examples of obtained UV/Vis spectra are presented.

According to the spectrophotometric results (see Table 3), it can be concluded that solutions of background electrolytes I and II reveal the best influence on extraction of dye from Hewlett-Packard ink on paper. Fortunately, these mixtures do not trigger destruction of the paper structure, hence the centrifuging stage of sample preparation could be minimized or even eliminated. In addition, the extracts based on both electrolytes can be directly injected into the capillary electrophoresis system without any additional treatment. What is more, further experiments with use of capillary electrophoresis system revealed that the transfer of paper modifiers to the extract

**Table 2:** Efficiency of extraction of three pure HP inks: Yellow (Y), Magenta (M) and Cyan (C) – visual evaluation.

No.	Extracting agent	Extraction efficiency (%) after								
		30 min			5 min of sonication			15 min of sonication		
		Y	M	C	Y	M	C	Y	M	C
1	Acetonitrile (ACN)	0	0	0	0	0	0	0	0	0
2	28% ammonia	25	50	50	25	75	50	50	100	50
3	Background electrolyte I *	50	75	75	75	100	75	75	100	100
4	Background electrolyte II **	25	50	50	50	75	75	75	75	100
5	Benzyl alcohol	0	0	0	0	0	0	0	0	0
6	2mM Brij-35 in water	25	50	50	50	75	50	75	100	75
7	Dichloromethane	0	0	0	0	0	0	0	0	25
8	Dimethylformamide (DMF)	50	50	50	75	75	75	75	100	75
9	DMF : water (1:1,v/v)	75	75	75	100	75	75	100	100	100
10	Dimethyl sulphoxide (DMSO)	75	50	75	75	50	75	100	75	100
11	DMSO : water (1:1,v/v)	50	50	75	75	75	75	75	100	100
12	Ethanol (EtOH)	0	0	0	0	0	0	0	25	0
13	Ethanol : pyridine (1:1,v/v)	25	0	0	25	0	0	25	25	25
14	Ethanol : water (1:1,v/v)	75	50	25	75	75	50	100	100	75
15	Ethanol : pyridine : water (1:1:1,v/v/v)	50	0	50	75	0	50	75	25	50
16	HCl : methanol (35:65, v/v)	75	25	0	75	50	25	100	75	50
17	Isopropanol	0	0	0	0	0	0	0	0	0
18	Citric acid (10%)	0	50	25	0	75	50	0	75	75
19	Methanol (MeOH)	50	25	25	75	25	25	100	25	25
20	Methoxyethoxyethanol (MEE)	25	25	25	25	25	25	25	25	25
21	MEE : water (1:1,v/v)	50	50	50	75	75	50	100	100	100
22	Pyridine	25	0	0	25	0	0	25	0	0
23	Pyridine : water (1:1,v/v)	75	75	75	75	75	75	100	100	100
24	Pyridine : acetic acid (1:1,v/v)	0	25	0	25	25	0	50	25	0
25	Pyridine : acetic acid (3:1,v/v)	25	0	0	25	0	0	25	25	25
26	Water	0	50	50	50	75	50	75	100	50

\* solution of 40 mM borate buffer with 20 mM SDS and 10% acetonitrile

\*\* solution of 80 mM borate buffer with 50 mM SDS and 10% methanol

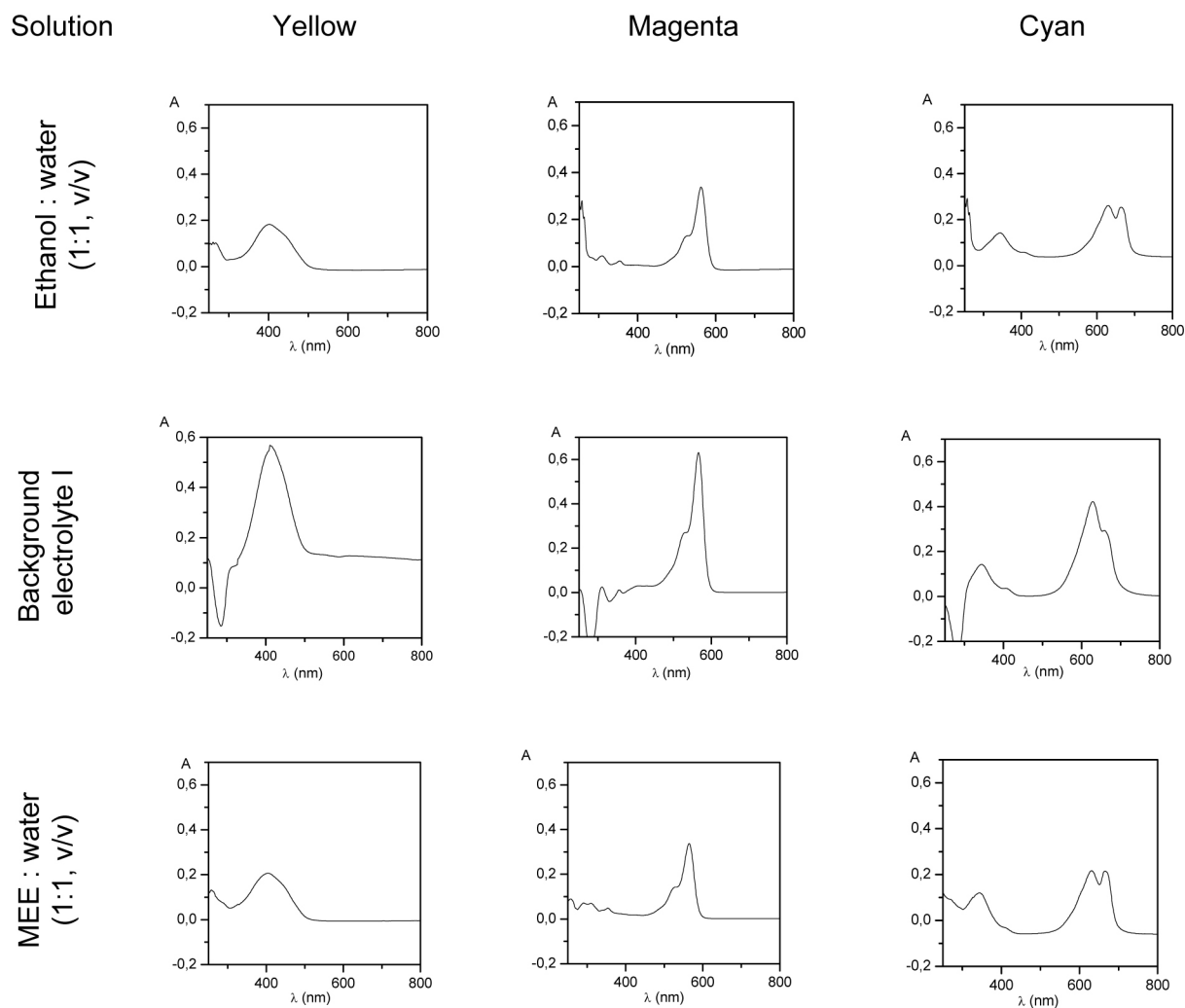


Figure 1. Example of UV/Vis spectra of Hewlett-Packard inks (Yellow, Magenta, Cyan) extracted by different extractants.

Table 3: Extraction efficiency of pure HP inks from paper – spectrophotometric evaluation.

No.	Extracting solution	Integrated area (a.u.)			Mean
		Yellow	Magenta	Cyan	
1	28% ammonia	11.8	12.9	13.3	12.7
2	Background electrolyte I	44.1	31.2	36.6	37.3
3	Background electrolyte II	32.2	32.5	33.3	32.6
4	2mM Brij-35 in water	16.7	13.1	18.3	16.0
5	DMF	11.5	14.4	20.2	15.3
6	DMF : water (1:1,v/v)	13.6	14.5	17.2	15.4
7	DMSO	18.1	12.0	20.8	17.0
8	DMSO : water (1:1,v/v)	12.1	13.4	25.9	17.1
9	Ethanol : water (1:1,v/v)	17.1	16.6	20.0	17.9
10	HCl : methanol (35:65,v/v)	23.3	17.9	14.4	18.5
11	MEE : water (1:1,v/v)	18.2	16.2	25.7	20.0
12	Pyridine : water (1:1,v/v)	12.9	13.5	21.0	15.3
13	Water	5.3	13.0	13.0	10.4
14	DMF : DMSO : EtOH : MEE : water (1:1:1:1:1, v/v/v/v/v)	14.0	23.4	16.2	17.9

is limited and the interference of optical brightener is lower.

Apart from the background electrolytes and water and ammonia, all other extractants affected inks to a similar extent (mean values of integrated area were between 15.0 and 20.0 a.u.). Among these, MEE with water was most effective, but DMSO and ethanol mixed individually with water as well as a mixture of DMF, DMSO, EtOH, MEE with water gave only slightly worse results. A relatively good effect was also obtained by the use of a solution of hydrochloric acid in methanol, but this was only due to high signals measured for Magenta and Yellow but not Cyan inks. Besides, this solution could create problems during CE separation because of a significant influence on electroosmotic flow.

Taking the above-presented results into account, four extracting agents: background electrolyte I, background electrolyte II, MEE with water and mixture of DMF, DMSO, EtOH and MEE with water were selected for further examinations.

### 3. 2. Efficiency of Mixed Inks Extraction

According to the results presented in Table 4, the mixtures of borate buffer with addition of surfactant and organic solvents were the most effective for all inks produced by Hewlett-Packard. What is more, all inks were extracted by these extracting agents to a similar extent. The point is that all of them are produced on the basis of the same or very similar colourants, which are contained in different inks in similar proportions. For instance, the main dyes of Cyan and Magenta inks are substituted phthalocyanine salts and naphthalene sulphonate salts respectively. In the case of Yellow ink, an acryl pirazol sul-

phonate salts or substituted naphthalene sulphonate salts are used as colouring matters but apparently they are similarly susceptible to both extracting mixtures based on borate buffer. Unfortunately, there is no possibility of comparing compositions in more detail because they are trade secrets.

All other inks were extracted better by a mixture of DMF, DMSO, EtOH and MEE with water than by both electrolytes. In the case of the Canon printer, this difference was not so great, but for inks produced by Brother, Epson and Lexmark, a mixture of organic solvents with water was definitely the best. This allows authors to assume that the chemical formula of inks produced by all of these manufacturers differs to a greater or lesser extent from that of HP inks. Moreover, it can be observed that the extraction efficiency revealed by all tested extractants in relation to inks of the same producer can also be quite different (compare results obtained for Pixma iP4500 and Pixma MP210, Stylus D92 and Stylus Photo R340, and Lexmark x2530 and Lexmark Z615).

A very exceptional case is ink taken from printer Stylus D92 (produced by Epson), which was much less affected by all extracting agents than every other ink. However, it was extracted much better by a mixture of four organic solvents with water than by electrolytes and also a single organic solvent (MEE) with water. The reason is that this is the only ink produced by the manufacturer for use in high quality printouts (in contrast to Stylus Photo R340 ink by the same producer) and its most characteristic feature is significant resistance to water.

It is seen in Table 4 that the mixture of MEE with water is generally less effective than the solution containing, additionally, DMF, DMSO and EtOH. Apparently, the presence of additional organic components ma-

**Table 4:** Extraction efficiency of inks extracted by four selected agents from rainbow printouts made by printers of different producers.

Company	Printer	Mean of integrated areas (a.u.)			
		Background electrolyte I	Background electrolyte II	MEE:H <sub>2</sub> O	DMF:DMSO:EtOH:MEE:H <sub>2</sub> O
Hewlett-Packard	Deskjet 930C	38.0	35.0	22.0	24.8
	Deskjet 895 Cxi	39.4	35.4	21.0	22.1
	Deskjet 950C/952C/959C	44.9	39.8	24.2	28.0
	Business Inkjet 1200	38.4	34.6	15.3	18.6
	Office Jet 5610	37.6	37.2	24.2	27.1
Canon	Pixma iP4500	22.9	21.5	18.9	25.2
	Pixma MP210	14.0	14.1	15.5	16.5
	Pixma iP1800	16.7	14.7	16.3	17.7
Brother	DCP-135C	28.9	27.8	31.4	44.5
	DCP-130C	27.9	38.9	33.3	39.1
	MFC-215C	38.7	19.3	40.2	41.9
Epson	Stylus D92	0.4	1.6	0.2	8.5
	Stylus Photo R340	47.6	18.8	46.6	59.4
Lexmark	Lexmark x2530	14.8	14.1	27.2	32.8
	Lexmark Z615	10.2	9.5	16.9	17.6

**Table 5:** Extraction efficiency of inks extracted by selected agents from rainbow printouts, which were made by two Hewlett-Packard printers equipped with two different cartridges (C6578 and C1823) and by two Canon printers equipped with the same ink cartridge (CL-38).

Extracting solution	Printer	Integrated area (a.u.)		
		Yellow	Magenta	Cyan
Background electrolyte I	Deskjet 930C	34.9	40.7	38.4
	Deskjet 895Cxi	36.9	45.1	37.1
Background electrolyte II	Deskjet 930C	33.3	37.1	34.7
	Deskjet 895Cxi	31.5	42.1	32.4
MEE:H <sub>2</sub> O	Deskjet 930C	17.7	24.0	24.3
	Deskjet 895Cxi	19.4	21.1	22.4
DMF:DMSO:EtOH:MEE:H <sub>2</sub> O	Deskjet 930C	19.0	25.8	29.6
	Deskjet 895Cxi	23.2	20.1	23.1
Background electrolyte I	Pixma MP210	0.2	21.0	20.8
	Pixma iP1800	2.6	24.0	23.3
Background electrolyte II	Pixma MP210	0.6	19.4	22.2
	Pixma iP1800	0.7	20.0	23.4
MEE:H <sub>2</sub> O	Pixma MP210	10.0	19.2	17.1
	Pixma iP1800	11.4	20.3	17.2
DMF:DMSO:EtOH:MEE:H <sub>2</sub> O	Pixma MP210	0.2	21.0	20.8
	Pixma iP1800	9.2	19.9	24.1

kes the extraction strength of a mixture greater even if an ink is not very resistant to water. Another observation is that both electrolytes are capable of acting very similarly as extractants and even if they are worse than the mixture of organic solvents they are able to ensure good extraction efficiency in relation to most of the inks examined (except StylusD92 and both inks produced by Lexmark).

Ink taken from two different printers (Pixma MP210 and Pixma iP1800) equipped with the same cartridge was extracted by all of the extracting agents with a very similar efficiency, measured not only by the mean value of integrated areas (see Table 4) but also by individual values obtained for Yellow, Magenta and Cyan dyes (see Table 5). This shows that if ink is extracted twice in the same conditions, the repeatability of the extraction efficiency can be expected to be very good even if the ink is taken from different printers (if printer settings are the same). However, two different inks can also be extracted by a given extractant with similar efficiency if these inks are taken from printers made by the same producer (compare results shown in Tables 4 and 5 for Deskjet 930C and Deskjet 895Cxi printers). The case that two different inks of different producers would be extracted by an extractant to a similar extent (measured by integrated area obtained for individual dyes) seems to be doubtful.

## 4. Conclusions

The presented results show that the best extractants for extraction of inkjet printer inks from paper are mixtures: a) 40 mM borate buffer with 20 mM SDS and 10% acetonitrile, and b) 80 mM borate buffer with 50 mM SDS

and 10% methanol. Either of them can be used as they reveal similar extraction efficiency and they can serve as background electrolytes for CE analysis. The great advantage of this extraction approach is the possibility of avoiding physical destruction of the paper, which is an undesired self-activating process observed in some organic solutions. As both solutions can be directly injected into the CE system without any additional treatment, their use contributes to saving time and effort during preparation of the ink sample for analysis by CE as well as to minimizing the risk of sample contamination.

If an ink is not well isolated from paper with the use of a solution based on borate buffer, it is recommended to use a solution containing DMF, DMSO, EtOH and MEE with water mixed all together with a volume ratio 1:1:1:1:1. A drawback of this solution is that it has to be evaporated before CE analysis as it can affect EOF, and give additional high intensity peaks (e.g. DMSO absorbs radiation in the UV range). However, it is necessary to use it in some special cases, e.g. when the ink examined is resistant to water.

It is worth noting that none of the extracting agents recommended above was proposed in the literature for extraction of inks before CE analysis.

The results obtained indicate some benefits in the use of two extractants – an electrolyte and an organic solution – simultaneously for initial examination of inkjet printing ink before of using CE for more detailed examination. The conditions are that a sufficiently large piece of a document printed by colour ink is available and the document can be destroyed to a relatively great extent (according to UV/Vis spectrophotometry sample requirement). If these conditions have been fulfilled, the following conclusions that are important from the forensic point of view

can be drawn after spectrophotometric measurements of extracts:

- if the extraction efficiency revealed by the electrolyte is greater than by organic solution, it can be assumed that the ink examined is produced by Hewlett-Packard,
- if the extraction efficiency is very low and it is revealed more by organic solution than by electrolyte, the ink examined is resistant to water (e.g. Epson Stylus D92),
- if two inks are examined (e.g. as evidence and reference samples) and both extracting agents extract them with approximately equal efficiency measured for Yellow, Magenta and Cyan dyes, there is a high probability that samples was taken from the same or the same type of cartridge made by the same producer (group identification),
- if two inks are examined and both extractants extract them with different efficiency, there is a high probability that both inks are taken from different printers (producers).

So, the extraction procedure developed in this paper has to be considered either – with special attention – as the preparative stage of CE analysis performed for forensic purposes or – in special circumstances – as a source of potential adjunctive but general information that facilitates the additional confirmation for the CE results. The above-outlined procedure could be reliable enough to be used on its own only after taking into account its reliability and additional studies including a wider sample set of inks from various manufacturers.

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## Povzetek

Zmožnost razlikovati med črnili za tiskalnike je velikega pomena pri preiskovanju dokumentov. Cilj tega dela je bil razviti postopek za učinkovito ekstrakcijo črnila z namenom nadaljnje analize s kapilarno elektroforezo. Spreminjali smo vrsto in sestavo ekstrakcijskih mešanic, kakor tudi čas ekstrakcije in čas izpostavljenosti ultrazvoku. Uporabili smo set različnih mešanic za ekstrakcijo črnil za tiskalnike Hewlett-Packard, Canon, Brother, Epson in Lexmark. Učinkovitost ekstrakcije smo ocenili vizualno in nato še s pomočjo UV/Vis spektrometrije. Ugotovili smo, da sta najbolj primerna ekstrakcijska reagenta mešanici boratnega pufra z SDS in acetonitrilom ali alternativno z metanolom, kar je obakrat ustrezen elektrolit za nadaljnjo CE analizo. Vendar pa so bile nekatere izjeme, ko smo visoko učinkovitost ekstrakcije dosegli z mešanico DMF, DMSO, EtOH in MEE z vodo.