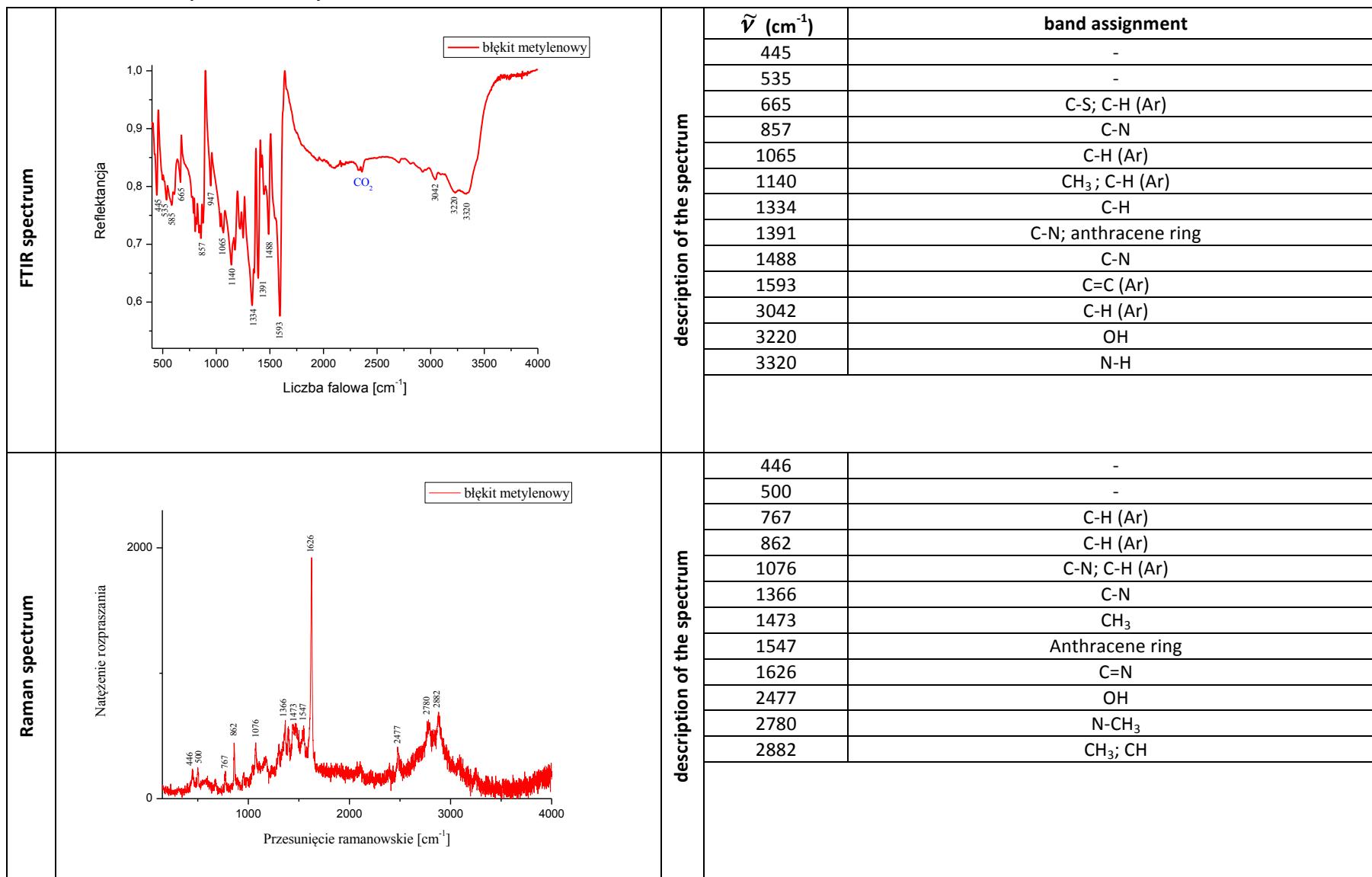
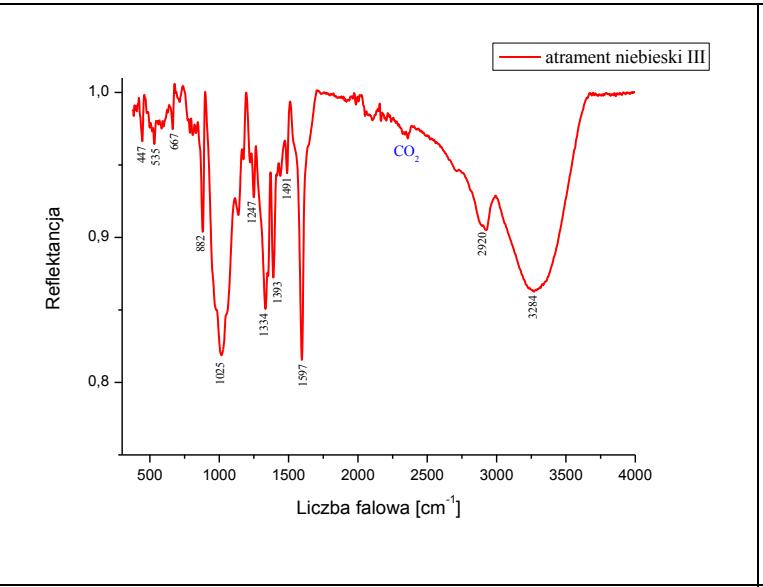


**Table 3. FTIR and Raman spectra of methylene blue**

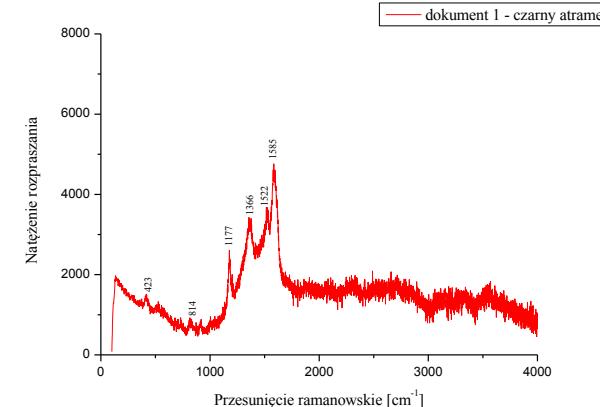
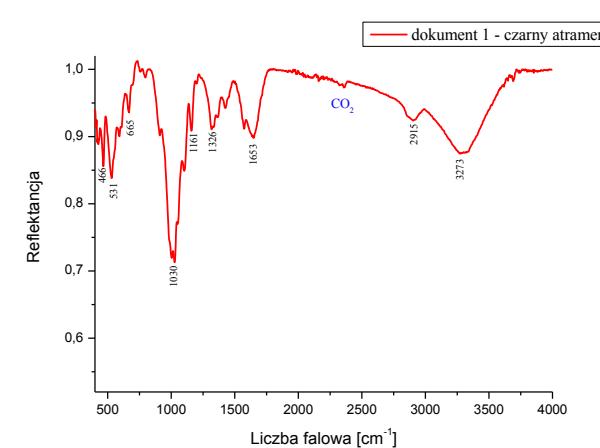


**Table 4. FTIR and Raman spectra of methylene blue ink**

FTIR spectrum	description of the spectrum	$\tilde{\nu}$ (cm <sup>-1</sup> )	band assignment	identification
	description of the spectrum	447	-	-
		535	-	-
		667	C-S; C-H (Ar); O-H	Methylene blue
		882	C-H (Ar)	Methylene blue
		1025	C-H (Ar); C-O	Methylene blue; gum arabic
		1247	C-H (Ar); C-O	Methylene blue; gum arabic
		1334	C-H	Methylene blue
		1393	C-N; anthracene ring	Methylene blue
		1491	C-N	Methylene blue
		1597	C=C (Ar); O-H	Methylene blue; gum arabic
		2920	C-H	Methylene blue; gum arabic
		3284	O-H	gum arabic
Raman spectrum	description of the spectrum	446	?	gum arabic
		500	?	gum arabic
		767	C-H (Ar)	Methylene blue
		862	C-H (Ar)	Methylene blue
		1076	C-N; C-H (Ar)	Methylene blue / gum arabic
		1031	C-N	Methylene blue
		1366	C-H (Ar)	Methylene blue
		1473	CH <sub>3</sub>	Methylene blue
		1547	anthracene ring	Methylene blue
		1626	C=N	Methylene blue
		2477	OH	Methylene blue
		2780	N-CH <sub>3</sub>	Methylene blue
		2878	CH <sub>3</sub> ; CH	Methylene blue

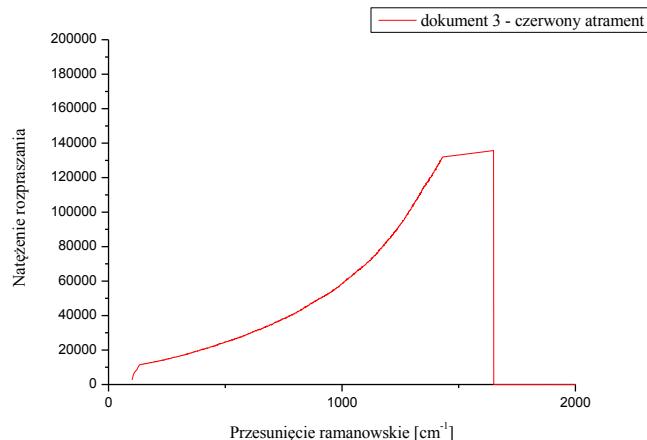
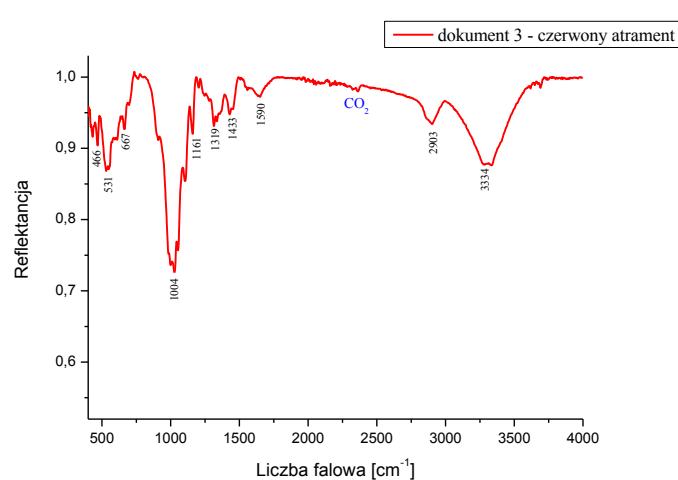
**Table 5. FTIR and Raman spectra of a historic document n°1 (black ink) from Cyprian Norwid Library in Elbląg, Poland**

FTIR spectrum	description of the spectrum	$\tilde{\nu}$ (cm <sup>-1</sup> )	band assignment	identification
		466	-	-
		531	-	-
		665	cellulose	Paper
		1030	cellulose; C-H (Ar); C-H (pyridine ring)	Paper; Leonhardi's patented ink
		1161	cellulose	Paper
		1326	cellulose; C-N; SO <sub>3</sub> <sup>2-</sup>	Paper; Leonhardi's patented ink
		1653	cellulose	Paper
		2915	cellulose	Paper
Raman spectrum	description of the spectrum	3273	cellulose; O-H; SO <sub>4</sub> <sup>2-</sup>	Paper; Leonhardi's patented ink
		423	cellulose	Paper
		814	cellulose; C-H (Ar)	Paper; Leonhardi's patented ink
		1177	cellulose; C-H (Ar)	Paper; Leonhardi's patented ink
		1366	cellulose	Paper
		1522	cellulose	Paper
		1585	cellulose; C=C (Ar); pyridine ring	Paper; Leonhardi's patented ink



**Table 6. FTIR and Raman spectra of a historic document n°3 (red ink) from Cyprian Norwid Library in Elbląg, Poland**

FTIR spectrum	description of the spectrum	$\tilde{\nu}$ (cm <sup>-1</sup> )	band assignment	identification
		466	-	-
		531	-	-
		667	cellulose	Paper
		1004	cellulose; C=C (Ar)	Paper; aniline red
		1161	cellulose	Paper
		1319	cellulose	Paper
		1433	cellulose; C-N	Paper; aniline red
		1590	C=C (Ar); N-H; C=N	aniline red
		2903	cellulose	Paper
Raman spectrum	description of the spectrum	3334	cellulose	Paper
		200000	identification was impossible due to extremely high fluorescence emission of the analysed material	



**Table 7. Results of optical and spectrometric analyses of reference inks and historic inks**

Analyzed material		Ink type	Ink colour in VIS	nIR reflectography	UV fluorescence	IR false colour	Results of analysis	
							FTIR	microRaman
<b>Methylene blue ink</b>	<b>basic</b>	synthetic	dark blue	Light gray, 25,10%÷37,30% IR absorbance range	No luminescence	Dark red	Methylene blue, gum arabic	Methylene blue, gum arabic
	<b>copying</b>	synthetic	light blue	Light gray, 27,06%÷40,78% IR absorbance range	No luminescence	Magenta	not analyzed	
<b>Fuchsine ink (red)</b>	<b>basic</b>	synthetic	pink	Close to transparent, 2,75%÷17,05% IR absorbance range	Medium emission intensity, dark pink colour	bright yellow	Fuchsine, gum arabic	Fuchsine, gum arabic
	<b>copying</b>	synthetic	Light pink	Close to transparent, 2,75%÷17,05% IR absorbance range	Medium emission intensity, light pink colour	Light yellow	not analyzed	
<b>Methyl violet ink</b>	<b>basic</b>	synthetic	violet	Close to transparent, 0,39%÷11,37% IR absorbance range	Low emission intensity, dark red colour	orange	Crystal Violet, glucose/fructose, oxalic acid	fluorescence
	<b>copying</b>	synthetic	Dark violet	Close to transparent, 11,37%÷29,41% IR absorbance range	Low emission intensity, dark red colour	Dark orange	not analyzed	
<b>Malachite green ink</b>	<b>basic</b>	synthetic	Cool blue	transparent	Low emission intensity, green colour	Cool pink	Malachite green	fluorescence
	<b>copying</b>	synthetic	Warm blue	transparent	Medium emission intensity, green colour	Warm pink	not analyzed	
<b>Nigrosine ink (Black)</b>	<b>basic</b>	synthetic	Dark gray	Dark gray, 65,49%÷88,24% IR absorbance range	No luminescence	Grayish green	nigrosine	fluorescence

	<b>copying</b>	synthetic	gray	Dark gray, 52,55%÷88,63% IR absorbance range	Low emission intensity, dark red colour	Grayish brown	not analyzed	
<b>Indigo carmine ink</b>	<b>basic</b>	synthetic	Dark blue	Transparent	No luminescence	red	Indigo carmine, gum arabic	Indigo carmine, gum arabic
	<b>copying</b>	synthetic	Dark blue	Transparent	Low emission intensity, violet colour	Light red	not analyzed	
	<b>alizarin ink</b>	natural	Warm dark gray	Dark gray, 56,08%÷81,96% IR absorbance range	low emission intensity, dark blue colour	like VIS	Indigo carmine, iron gallates, oxalic acid, gum arabic, acetic acid	iron gallates, gum arabic
	<b>iron-gall ink with logwood</b>	natural	Dark Brown	Dark gray, 62,35%÷80,78% IR absorbance range	Very low emission intensity, dark blue colour	Brown red	iron gallates, haematein	iron gallates, gum arabic, haematein
	<b>logwood ink</b>	natural	Cool dark Brown	Dark gray, 62,00%÷85,10% IR absorbance range	No luminescence	Brown red	haematein	haematein, potassium chromate
	<b>Leonhardi's patented ink</b>	natural	black	Dark gray, 58,82%÷84,71% IR absorbance range	No luminescence	Brown red	indigo carmine, iron gallates, alizarin, acetic acid	indigo carmine, iron gallates, alizarin, acetic acid
<b>Pencil n° 1</b>	<b>dry</b>	synthetic	violet	light gray, 25,49%÷49,41% IR absorbance range	low emission intensity, dark blue colour	red	methylene blue, kaolin	methylene blue
	<b>water dissolved</b>	synthetic	blue	transparent	Very low emission intensity, dark blue colour	pink	not analyzed	
<b>Pencil n° 2</b>	<b>dry</b>	synthetic	warm gray	dark gray 29,02%÷69,02% IR absorbance range	medium emission intensity, blue colour	like VIS	kaolin, methyl violet	kaolin, methyl violet
	<b>water dissolved</b>	synthetic	violet blue	dark gray, 21,57%÷53,33% IR absorbance range	medium emission intensity, violet colour	red	not analyzed	

Pencil n° 3	<b>dry</b>	synthetic	light green	dark gray, 52,16%÷79,22% IR absorbance range	low emission intensity, dark green colour	violet blue	prussian blue, aniline yellow, kaolin	prussian blue, aniline yellow, kaolin
	<b>water dissolved</b>	synthetic	light green	dark gray, 27,84%÷51,37% IR absorbance range	medium emission intensity, dark green colour	violet blue	not analyzed	
Pencil n° 4	<b>dry</b>	synthetic	warm gray	dark gray, 62,35%÷76,08% IR absorbance range	medium emission intensity, blue colour	like VIS	methyl violet, kaolin	methyl violet, kaolin
	<b>water dissolved</b>	synthetic	violet blue	gray, 45,88%÷62,35% IR absorbance range	low emission intensity, violet colour	violet red	not analyzed	
Pencil n° 5	<b>dry</b>	synthetic	warm gray	dark gray, 14,12%÷60,39% IR absorbance range	very low emission intensity, dark blue colour	like VIS	methyl violet, kaolin	methyl violet, kaolin
	<b>water dissolved</b>	synthetic	violet blue	dark gray, 30,98%÷50,20% IR absorbance range	low emission intensity, violet colour	violet red	not analyzed	
Pencil n° 6	<b>dry</b>	synthetic	warm gray	dark gray, 14,51%÷63,92% IR absorbance range	no luminescence	cool gray	methylene blue, kaolin	methylene blue, kaolin
	<b>water dissolved</b>	synthetic	green blue	dark gray, 26,27%÷58,82% IR absorbance range	no luminescence	pink violet	not analyzed	
Pencil n° 7	<b>dry</b>	synthetic	warm gray	dark gray, 21,96%÷55,70% IR absorbance range	medium emission intensity, dark blue colour with grayish shade	like VIS	methyl violet, kaolin	methyl violet, kaolin
	<b>water dissolved</b>	synthetic	violet	dark gray, 26,27%÷51,37% IR absorbance range	low emission intensity, dark violet colour	brown yellow	not analyzed	
Pencil n° 8	<b>dry</b>	synthetic	violet blue	transparent	very low emission intensity, dark blue colour	red	methylene blue, kaolin	methylene blue, kaolin

	<b>water-dissolved</b>	synthetic	violet blue	transparent	very low emission intensity, dark blue colour	red	not analyzed	
<b>document n° 1</b>	<b>black ink</b>	synthetic	brown	light gray, 11,37%÷49,80% IR absorbance range	no luminescence	brown red	paper, Leonhardi's patented ink	paper, Leonhardi's patented ink
	<b>gray blue ink</b>	synthetic	grayish blue	almost transparent, 12,16%÷30,20% IR absorbance range	very low emission intensity, blue colour	light red	paper	fluorescence
	<b>blue pencil</b>	synthetic	violet blue	transparent	medium emission intensity, blue colour	violet red	paper, methylene blue	fluorescence
	<b>gray pencil</b>	synthetic	warm gray	dark gray, 54,51%÷76,08% IR absorbance range	medium emission intensity, blue colour	violet red	paper, methylene blue	fluorescence
<b>document n° 2</b>	<b>violet pencil</b>	synthetic	light violet	almost transparent, 9,09%÷25,10% IR absorbance range	high emission intensity, dark blue colour	light red	paper, methylene blue	fluorescence
<b>document n° 3</b>	<b>red ink</b>	synthetic	orange red	transparent	medium emission intensity, dark pink colour	bright yellow	paper, aniline red	fluorescence
<b>document n° 4</b>		synthetic	violet	transparent	medium emission intensity, blue colour	orange red	paper, aniline violet	fluorescence