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Pilot Study of the Qualitative Analysis of Urinary Stones by Near Infrared Spectroscopy and Chemometrics

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Abstract: Urolithiasis is one of most common urogenital diseases. Its diagnosis and treatment require an efficient analytical method of determination of chemical composition of a urinary stone, ideally, during the surgery. Near infrared spectroscopy seems to be a promising method for intraoperative qualitative analysis of urinary stones (calcium oxalates, uric acid, etc.), providing fast measurements and portable equipment. In this work, the results of a pilot study of analyzing several urinary stones with different chemical composition (dry and soaked in saline) within the 939-1799 nm range are presented. The Principal Component Analysis results confirm the potential of this technique in qualitative analysis of urinary stones before their surgical removal.

Keywords: urinary stones; near infrared spectroscopy; urology

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1. Introduction

Diseases of the urogenital system have a significant impact on the quality of life. Timely measures for early diagnosis and reduction of the risk of disease recurrence are impossible without a developed complex of methods of physical and chemical analysis of multicomponent biological samples (urine, urinary stones, etc.). With a variety of routine laboratory analyses, characterized by high accuracy, there is a lack of online methods, including intraoperative ones, which allow making effective medical decisions in real time.

Urolithiasis has a significant proportion among urogenital diseases. According to the clinical guidelines, the choice of treatment (conservative and surgical) and prevention of recurrence of urolithiasis is largely determined not only by the location and size of the stone, but also by its chemical composition [1]. At the same time, the recommendations do not give any reliable methods of determining the composition of a stone before its removal. CT scanning also has several disadvantages: firstly, some types of stones are not visualized on the images, secondly, tomography is associated with a radiation emission and cannot always be performed in every medical institution. Thus, the development of methods of qualitative analysis of urinary stones *in vivo* is important for both early diagnosis and screening of urolithiasis and for effective stone removal and control of the patient's condition after treatment.

The search for methods of determining the chemical composition of urinary and renal stones proceeds in several directions: improvement of computed tomography (CT) [2], use of machine learning for image processing and application of spectral methods [3]. Dual-energy CT is the most advanced technique for determining stone composition prior to stone removal, however, this method provides an answer only to the question "whether a stone contains uric acid or not". Moreover, the equipment for dual-energy CT is not widely available, and this method is associated with the increased radiation exposure compared with conventional CT, which limits its use.

Portable near-infrared spectrometers with fiber optic probes have a great potential for intraoperative qualitative analysis of urinary stones. First, the fiber optic probes are widely available, easy-to-implement and cost-effective. Second, the typical components of urinary stones are oxalates, phosphates, and uric acid, which give analytical signals in the near infrared range. Finally, this equipment is low-cost and does not require thorough sample preparation or specific reagents.

In this work, we present a pilot study of near infrared (NIR) measurements for several real samples of urinary stones, performed under different conditions (ambient atmosphere, saline). A portable NIR spectrometer with a halogen lamp and a flexible fiber optic probe was used in the range between 939 and 1799 nm in diffuse reflectance mode. The results of exploratory analysis of the measured spectra by principal component analysis (PCA) are presented, which prove the potential of this method in surgical treatment of urolithiasis.

2. Materials and Methods

The real samples of urinary stones with different composition (Table 1, the reference results were obtained by X-ray phase analysis) were measured under different conditions by a portable near-infrared spectrometer (AvaSpec-NIR256-1.7-USB2, Avantes) via a flexible fiber-optic probe. NIR spectra were registered in the range 939-1799 nm in diffuse reflectance mode (4-nm step); the acquisition time for one spectrum was 900 msec (including ten consecutive scans). A reference spectrum was measured from the reflectance standard (Spectralon®).

Table 1. Composition of the urinary stones under study.

Number	Composition
	Experiment No.1 with dry samples
1	Calcium oxalate monohydrate (100%)
2	Calcium oxalate monohydrate (100%)
3	Calcium oxalate monohydrate (100%)
4	Calcium oxalate monohydrate (100%)
5	Calcium oxalate monohydrate (100%)
6	Calcium oxalate monohydrate (100%)
7	Calcium oxalate monohydrate (100%)
8	Calcium oxalate monohydrate (85%) and dihydrate (15%)
9	Calcium oxalate monohydrate (95%) and carbonate apatite (5%)
10	Uric acid (100%)
11	Uric acid (100%)
12	Uric acid (90%) and its hydrate (10%)
	Experiment No.2 with samples soaked in saline
1	Uric acid (100%)
2	Uric acid (100%)
3	Uric acid (100%)
4	Uric acid (100%)
5	Uric acid (100%)
6	Calcium oxalate monohydrate (95%) and carbonate apatite (5%)
7	Calcium oxalate monohydrate (100%)
8	Calcium oxalate monohydrate (80%) and dihydrate (20%)
9	Calcium oxalate monohydrate (100%)
10	Calcium oxalate monohydrate (100%)

The measurements were performed within two experiments: under ambient atmosphere (dry samples) and in saline (0,9 g of NaCl, puriss., per 100 mL of distilled water) with permanent stirring to mimic the surgery conditions. The samples were soaked in saline during two hours before the corresponding measurements.

3. Results

3.1. Dry Samples

The NIR spectra of dry urinary stones after SNV processing are presented in Figures 1 (calcium oxalate stones) and 2 (uric acid). The difference between absorption patterns is evident: calcium oxalate stones have a broad complex signal between 1400-1800 nm, while uric acid is characterized by a peak at 1670 nm. However, the minor components of calcium oxalate stones (calcium oxalate dihydrate, carbonate apatite) cannot be clearly identified.

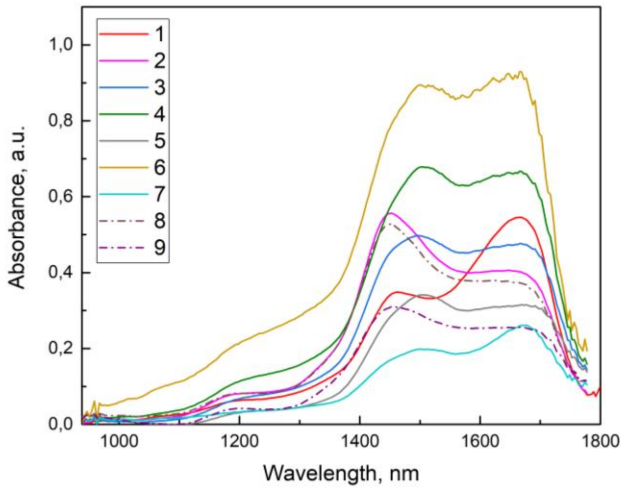

Figure 1. NIR spectra of calcium oxalate stones. Solid lines indicate the spectra of calcium oxalate monohydrate stones.

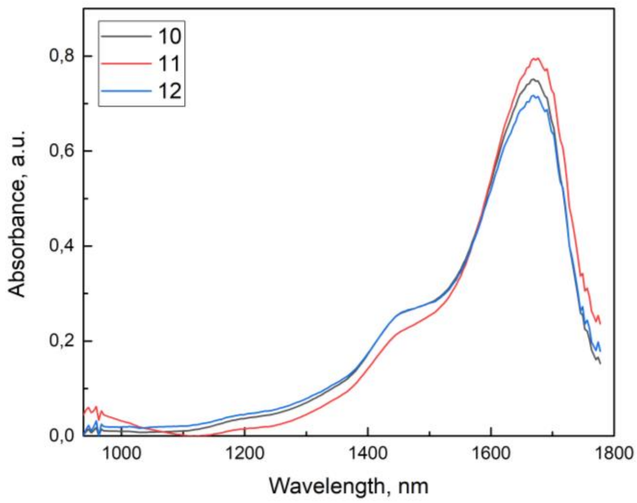

Figure 2. NIR spectra of uric acid stones.

The results of PCA (Unscrambler 9.7, Camo) confirm the possibility of distinction of two most common types of urinary stones (Figure 3). The samples of uric acid and calcium oxalate stones form two distant clusters.

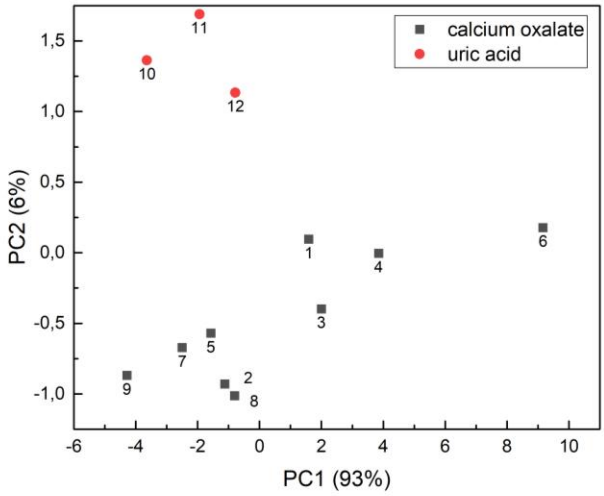

Figure 3. PCA scores plot for NIR spectra of dry urinary stones. Explained variances for each component are given in parentheses.

3.2. Samples in Saline

Five NIR spectra were measured in different sites of each of ten stones and averaged to take into account the effects caused by heterogeneous surface of a stone. Forty spectra of saline itself were also measured, averaged and used to calculate difference spectra ("stone" – "saline"). These spectra are shown in Figure 4. While the shape of the spectra was changed, the difference between two groups of stones remained, which is confirmed by PCA scores plot (Figure 5).

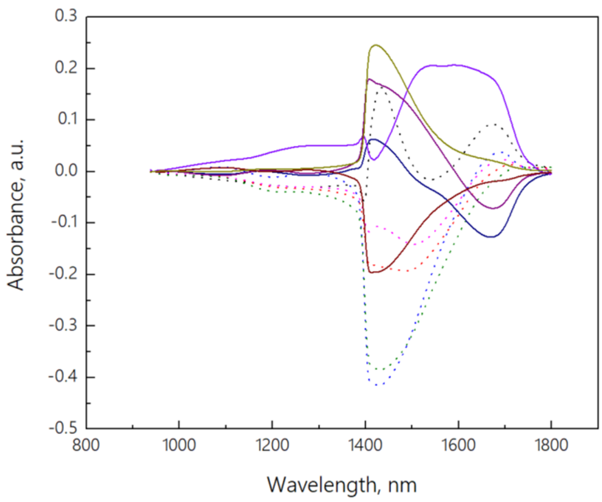

Figure 4. Difference NIR spectra of urinary stones, measured in saline. Solid lines indicate calcium oxalate stones, dot lines – uric acid stones.

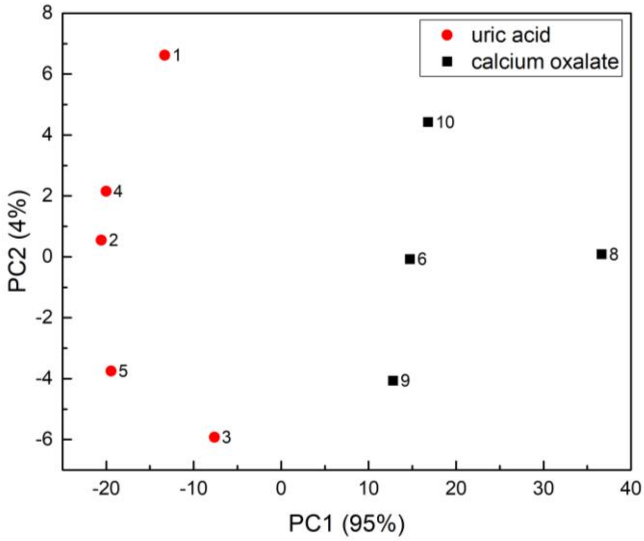

Figure 5. PCA scores plot for NIR spectra of urinary stones in saline. Explained variances for each component are given in parentheses.

4. Conclusion

The results of a pilot study, aimed to assess the potential of NIR spectroscopy in the intraoperative qualitative analysis of urinary stones, were presented. We demonstrated that it was possible to group calcium oxalate and uric acid stones into two separate clusters, based on their NIR spectra. Further research will include the experiments in real urine and during a lithotripsy surgery.

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