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Proceeding Paper

Pilot Study on the Qualitative Analysis of Urinary Stones Using 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 to determine the chemical composition of a urinary stone, ideally during surgery. Near-infrared spectroscopy seems to be a promising method for conducting intraoperative qualitative analysis on urinary stones (calcium oxalates, uric acid, etc.), providing fast measurements and portable equipment. In this study, the pilot study results based on analyzing several urinary stones with different chemical compositions (dry and soaked in saline) within the 939–1799 nm range are presented. Principal component analysis results confirm the potential of this technique in qualitatively analyzing 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 ensuring early diagnoses and reducing the risk of disease recurrence are impossible without a developed complex of physical and chemical analysis methods for 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 make effective medical decisions in real time.

Urolithiasis is a common type of urogenital disease. According to clinical guidelines, the choice of treatment (conservative and surgical) and the prevention of the recurrence of urolithiasis are not only largely determined by the location and size of the stone, but also by its chemical composition [1]. At the same time, 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 qualitative analysis methods for urinary stones in vivo is important for both the early diagnosis and screening of urolithiasis, effective stone removal, and the control of a patient's condition after treatment.

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

Portable near-infrared spectrometers with fiber optic probes have great potential for the intraoperative qualitative analysis of urinary stones. First, 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 study, we present a pilot study on near-infrared (NIR) measurements for several real samples of urinary stones, performed under different conditions (ambient atmosphere, saline, etc.). 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 exploratory analysis results on the measured spectra using principal component analysis (PCA) are presented and prove the potential of this method to be used in the surgical treatment of urolithiasis.

2. Materials and Methods

The real samples of urinary stones with different compositions (the reference results shown in Table 1 were obtained via X-ray phase analysis) were measured under different conditions using a portable near-infrared spectrometer (AvaSpec-NIR256-1.7-USB2, Avantes, Apeldoorn, the Netherlands) and 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 ms (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%)
A7	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 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 Figure 1 (calcium oxalate stones) and Figure 2 (uric acid). The difference between absorption patterns was evident: calcium oxalate stones had a broad complex signal between 1400 and 1800 nm, while uric acid was characterized by a peak at 1670 nm. However, the minor components of calcium oxalate stones (calcium oxalate dihydrate and carbonate apatite) could not be clearly identified.

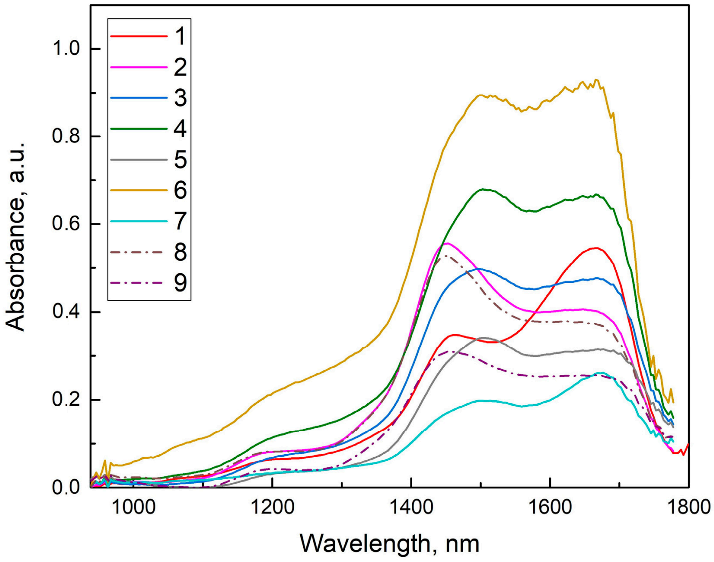

Figure 1. NIR spectra of calcium oxalate stones. Solid lines indicate the spectra of calcium oxalate monohydrate stones.

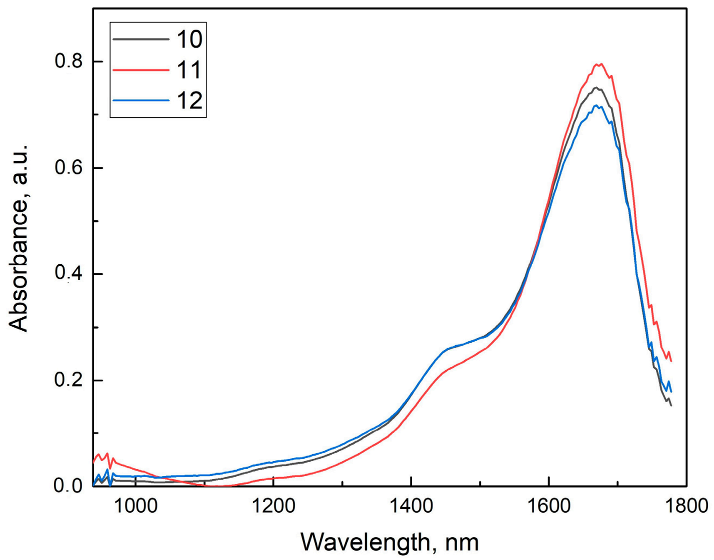

Figure 2. NIR spectra of uric acid stones.

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

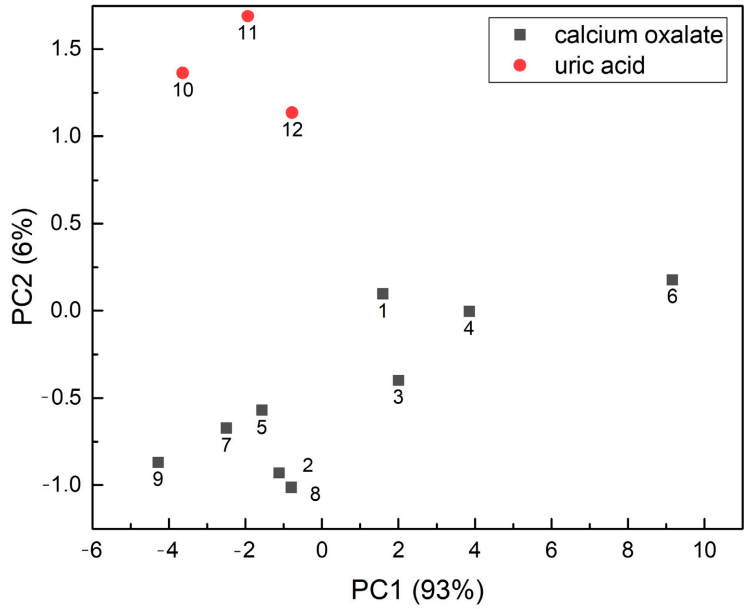

Figure 3. PCA score plot for NIR spectra of dry urinary stones. Explained variances for each component are given in parentheses.

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 the heterogeneous surface of a stone. Forty spectra of the 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, as confirmed by the PCA score plot (Figure 5).

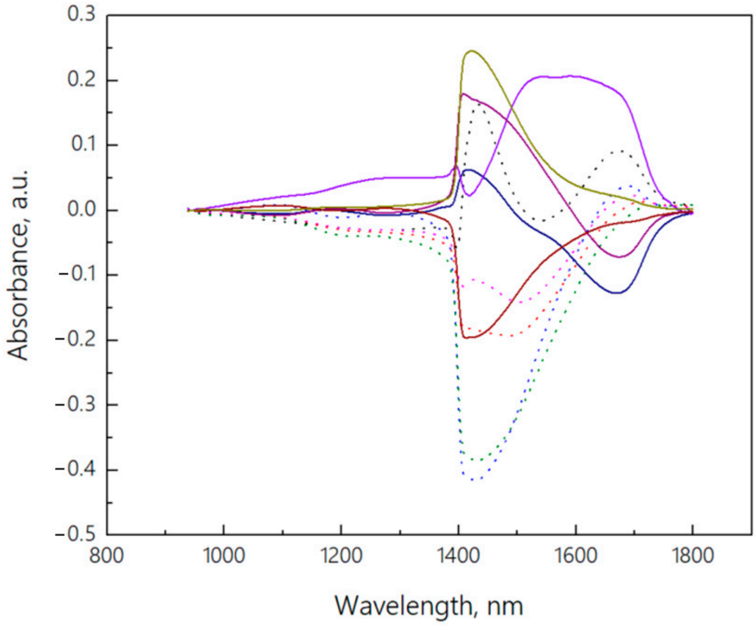

Figure 4. Difference NIR spectra of urinary stones, measured in saline. Solid lines indicate calcium oxalate stones, while dotted lines indicate uric acid stones.

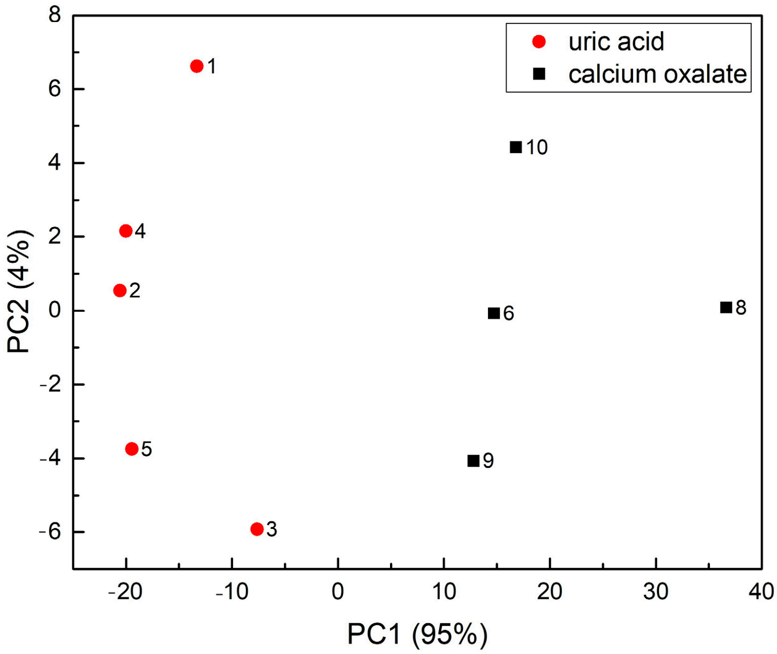

Figure 5. PCA score plot for the NIR spectra of urinary stones in saline. Explained variances for each component are given in parentheses.

4. Conclusions

The results of this 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 experiments on real urine during lithotripsy surgery.

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