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Stone analysis

Accepted: 8 November 2005 / Published online: 14 February 2006
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Abstract The definition and the frequencies of the components of urinary stones are presented on the basis of more than 110,000 analyses. The stone morphologies are described. The methods of stone analysis X-ray diffraction, infrared spectroscopy and polarization microscopy and the most recent developments are presented. The benefits and disadvantages of different methods are compared. The results of ring trials show that the X-ray diffraction method is the best method with regard to correctness.

Keywords Urinary stone analysis · X-ray diffraction · Infrared spectroscopy · Polarization microscopy · Stone morphology · Stone frequency

Definition of urinary stone

Urinary stones are solid biogenous formations of the urinary system. They mainly have a crystalline structure and the size is more than 1 mm. About 95% of stones are crystalline components and 5% are organic components, the so-called matrix or proteins.

Stone components

The most frequent components are the calcium oxalates, whewellite and weddellite as monohydrate and dihydrate. The occurrence frequency of whewellite is 78% and that of weddellite 43%.

The figures show the typical, different morphologies of both oxalates. Apatite is a very frequent component with 33%. Brushite is not so frequent with 1–2%, but the frequency of brushite has increased in recent years. The other calcium phosphates, such as whitlockite and octacalcium phosphate, are very rare (Figs. 1, 2).

The most typical infection stone component is struvite, a magnesium-ammonium phosphate hexahydrate with a frequency of 6%. Struvite often forms great staghorn stones with apatite. Newberyite is a very rare transformation product of struvite.

Uric acid is a frequent stone constituent with a frequency of 10%, as well as uric acid dihydrate with 6%. Uric acid monohydrate is seldom present. It was recently described by us for the first time (Figs. 3, 4).

Ammonium urate has a frequency of 1%. The other urates and purine derivatives, such as xanthine and dihydroxyadenine, are absolutely rare. Cystine is not so frequent with 0.3%. But it has great importance, because of the high recurrence rate without metaphylaxis (Figs. 5, 6).

For a survey on the occurrence frequency of stone components see Table 1.

Only seven components have a frequency more than 1%. The others, about 15 stone minerals, are rare up to very, very rare. Noteworthy is the percentage of artefacts with 2.3%.

The majority (44%) of our stones ($n = 70,131$) consist of two minerals, 34% have only one component, 22% consist of three minerals, only 0.7% consist of four, five or six components.

The fact that mixtures of stone components play a great role is important for stone analysis.

Purposes and problems

The purpose of stone analysis is the extensive qualitative differentiation of all stone components, especially of the different hydrate forms, the urates and purine derivatives and of the several calcium phosphates.

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Stone components 1

Calcium oxalates

Whewellite

$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ 78 %



Weddellite

$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ 43 %



Fig. 1 Stone components 1

Stone components 2

Calcium phosphates

Apatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{CO}_3)$ 33 %

Brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ 1.1 %

Whitlockite, OCP <1 %

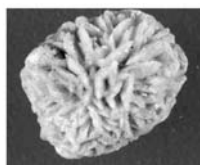


Fig. 2 Stone components 2

Stone components 3

Magnesium Ammonium Phosphates (Infection stones)

Struvite $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ 6 %

Newberyite $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ < 1 %



Fig. 3 Stone components 3

Stone components 4

Uric acid and -hydrates

Uric acid $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$ 10 %

Uric acid dihydrate $\text{C}_5\text{H}_4\text{N}_4\text{O}_3 \cdot 2\text{H}_2\text{O}$ 6 %

Uric acid monohydrate $\text{C}_5\text{H}_4\text{N}_4\text{O}_3 \cdot \text{H}_2\text{O}$ < 0.1 %

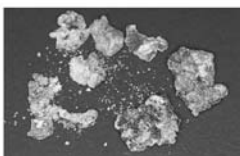


Fig. 4 Stone components 4

Table 1 Occurrence frequency of stone components ($n = 111,196$)

Component (%)

Whewellite	77.5
Weddellite	42.8
Apatite	32.5
Uric acid	10.0
Struvite	5.9
Uric acid dihydrate	5.5
Brushite	1.1
Ammonium urate	0.9
Cystine	0.3
Octacalcium phosphate	0.2
Whitlockite	0.1
Na-, K-urate	0.03
Newberyite	> 0.01
Calcite, aragonite	> 0.01
Drug stone	> 0.01
Organic	0.6
Artefacts	2.3

Stone components 5

Urates and other Purine derivatives

Ammonium-, Sodium-, Potassium urates 1 %

Xanthine, 2,8 Dihydroxyadenine < 1 %



Fig. 5 Stone components 5

Stone components 6

Cystine $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$ 0.3 %

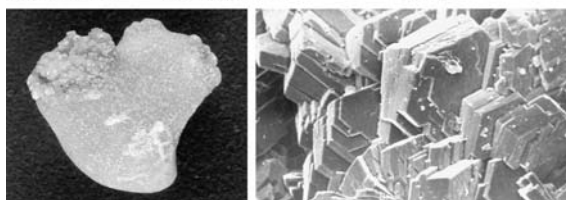


Fig. 6 Stone components 6

Another purpose is the semiquantitative determination of all components in mixtures.

A certain problem is the analysis of demanding stone phases, such as rare purine derivatives, drug-induced stones and artefacts in some cases.

The consideration of inhomogeneities (core-shell, disintegrates in stones) and problems of cost efficiency are important, too.

Polarization Microscopy

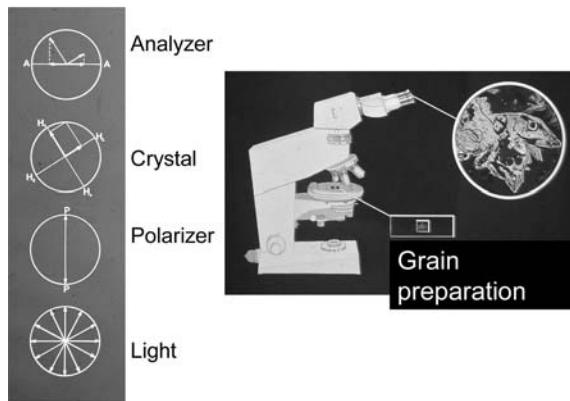


Fig. 7 Polarization microscopy

Stone analysis is of importance to the therapy and metaphylaxis of residual and recurrent stones:

- Composition and structure refer to the choice of therapy methods.
- Litholysis in the case of uric acid and struvite.
- The choice of URS or PCNL as alternative methods for ESWL-resistant stones such as whewellite, brushite and cystine.

Exact stone analysis is the basic requirement for an effective metaphylaxis!

Methods of stone analysis

The most used methods of stone analysis are

- Polarization microscopy on grain preparations
- X-ray diffraction
- Infrared spectroscopy
- Chemical methods in the form of analysis sets

Polarization microscopy

Polarization microscopy is based on the interaction of polarized light with the crystals of stones. The colour, refraction of light and double refraction are parameters for the identification of stone minerals (Fig. 7).

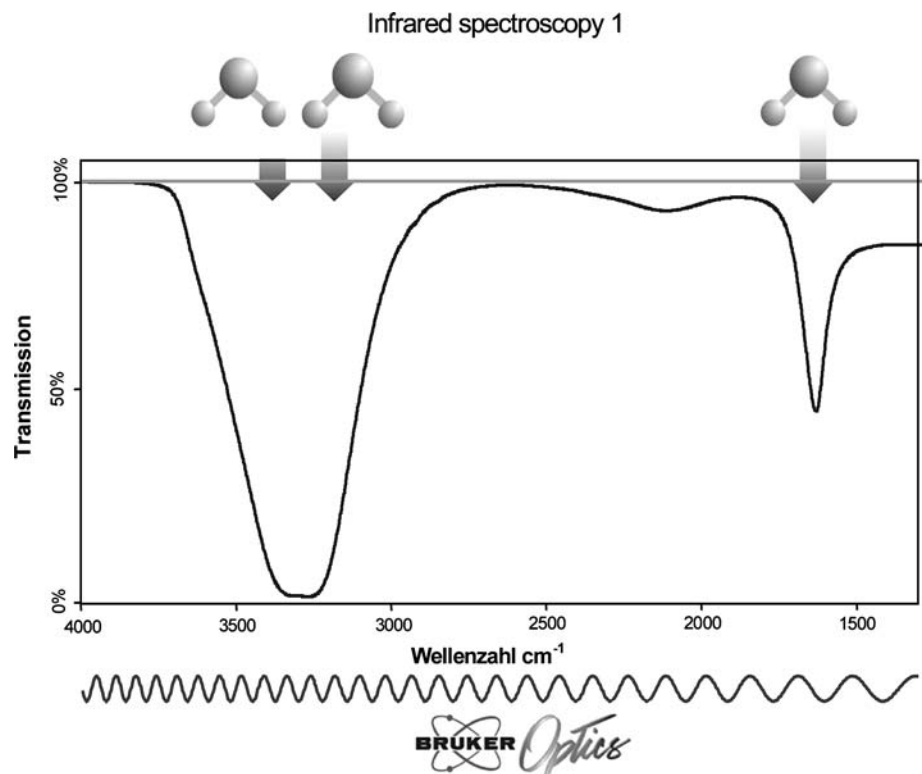
The benefits of polarization microscopy are:

- Cost efficiency.
- Quick examinations and analyses of very small samples are possible.
- This method is really the final analysis for simple stones such as whewellite or weddellite.
- Very small contents of components in the stones are detectable.

The disadvantages are:

- High subjective experience is necessary.
- Differentiation of components is difficult in some cases in the groups of uric acid and purine derivatives and calcium phosphates.
- The quantitative analysis in mixtures is difficult in some cases.

Fig. 8 Infrared spectroscopy 1



Infrared Spectroscopy 2

ATR – Technique: Attenuated Total Reflectance

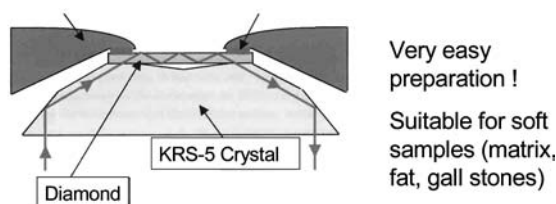


Fig. 9 Infrared spectroscopy 2

Infrared spectroscopy

Infrared spectroscopy is based on the interaction of the infrared light and the molecules in the stone components. The light stimulates atomic vibrations. The consequence is energy absorption, which results in absorption bands in the infrared spectrum.

A new technique in infrared spectroscopy is the method of attenuated total reflection—the diamond ATR method. The advantages of this technique are the very easy preparation and the application for soft samples (Figs. 8, 9).

The benefits of infrared spectroscopy are:

- Moderate costs.
- Very quick examination using FTIR technique.
- Examinations of small samples are possible.
- Preparation is very easy using ATR technique.
- Semiautomatic evaluations are possible applying search-match functions.
- Noncrystalline substances (as proteins or fat) are detectable.

The disadvantages are:

- Time-consuming preparation applying the usual tablets technique with potassium bromide.
- Differentiation and qualitative analyses are in some cases difficult, for example in the case of uric acid and purines and calcium phosphates.
- The detection of small contents of components is in some cases difficult, for example whewellite in

X – Ray Diffraction 1

Diffraction of X-rays on the crystal lattice

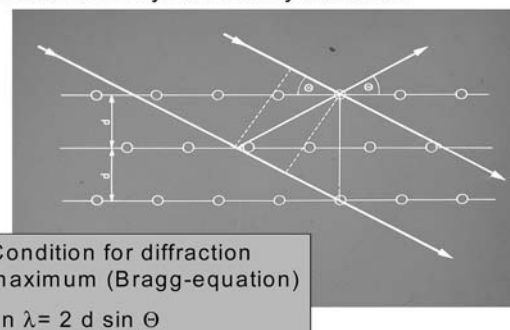


Fig. 10 X-ray diffraction 1

weddellite or reverse, or urates and uric acid dihydrate in uric acid and others.

X-ray diffraction

X-ray diffraction is based on the diffraction of X-rays on crystal lattice. Subject to certain conditions, there are diffraction maxima corresponding to the Bragg equation (Figs. 10, 11).

An X-ray equipment, used by our laboratory, is seen (Fig. 11, right) with the X-ray tube, the sample changer and the detector. Measurement of up to 12 samples is programmable.

An Autoquan program allows the exact and easy quantitative analysis of the stone components.

The benefits of this method are:

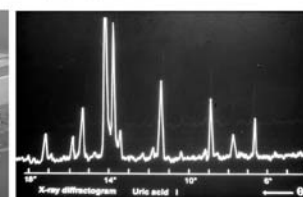
- Easy preparation.
- Automatic measurement (using a sample changer).
- Semiautomatic evaluation of the X-ray diffractogram (search-match program).
- Quantitative analyses (applying the Autoquan system).
- Exact differentiation of all crystalline components is possible.

Fig. 11 X-ray diffraction 2

X – Ray Diffraction 2



XRD 3003 with sample changer



Quantitative Analysis: Exact and easy by AutoQuan



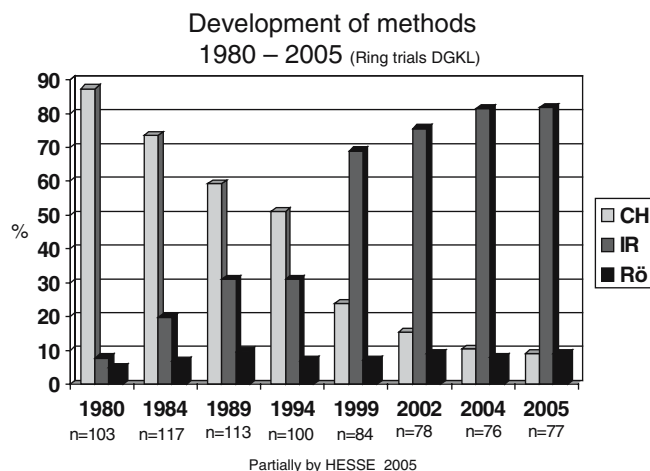


Fig. 12 Development of methods 1980–2005 (Ring trials DGKL)

The disadvantages are:

- High costs.
- Noncrystalline substances are not detectable.
- Time per measurement is up to 30 min.

Figure 12 shows the development of used methods from 1980 to 2005.

The data are based on the participants in the ring trials of the German Society of Clinical Chemistry. The data up to 2001 are provided by Hesse, the initiator and the scientific adviser of this ring trial up to 2001. The data show a decrease of the used chemical method from 87% in 1980 to 9% in 2005.

The use of infrared spectroscopy increased from 8% in 1980 to 81% in 2005. The use of X-ray diffraction has remained nearly constant at 5–9%.

A result of the survey for urinary stone analysis in the year 2003 (Fig. 13) is helpful for the evaluation of the different methods:

- The sample consisted of 60% brushite and 40% apatite.
- The qualitative correctness of the chemical method was 20% for brushite and 30% for apatite.
- Referring to infrared spectroscopy, 93% of the participants detected brushite correctly but only 60% detected apatite correctly.

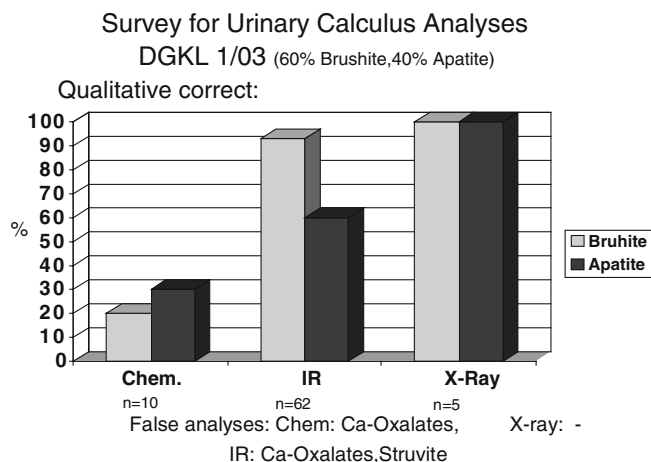


Fig. 13 Survey for urinary calculus analyses DGKL 1/03 (60% brushite, 40% apatite)

- Participants using X-ray diffraction detected brushite and apatite with 100% correctness.
- The results of the participants applying chemical methods and infrared spectroscopy display false analyses like calcium oxalates and struvite.
- The participants applying X-ray diffraction had no false analyses.

Current problems of stone analysis

- The results of the ring trials reveal that the quality of stone analysis is improvable in spite of using exact methods such as infrared spectroscopy.
- Unfortunately, many urologists do without stone analysis due to cost reasons, ignorance or convenience.

At least one stone analysis for each stone episode per patient is required for an effective therapy and metaphylaxis.