Quantitative Methods for Determination of Compositions of Kidney Stones Patients by Spectrophotometric Technique

Ali Moaid Abid-Alwahid, Hussein Hassan kharnoob, Hasan Ahmed Hasan

College of Pharmacy, University of Tikrit, Tikrit, Iraq

Abstract

In this research chemical compositions (calcium, magnesium, and inorganic phosphorus ions) of kidney stones using quantitative methods were determined. Forty three calculi [14 from female (32.6%) and 29 of male (67.4%)] were investigated using visible spectrophotometry at different wavelengths. The analytical quantitative methods used for determination the concentrations of these metals were accurate, reliable and sensitive with linear range of (5-65), (0.05-0.5), and (1.5-13.5) µg/ml and standard deviation 0.004596, 0.002390, and 0.000756 and low detection limit (L.O.D.) was 0.1120, 0.0177, and 0.1890 µg/ml while the (RSD) was 1.40%, 2.36%, and 5.04% respectively.The most found kidney stones were either rigid or soft with different shapes and colures. The stones were digested with three solutions [1N HNO_3, 16.5N HNO_3, and de-ionized water (D.I.W)], the highest concentrations of the Ca, Mg, and P were found at 16.5N HNO_3 digest solution.

Keywords: Renal stone, urinary system, quantitative methods, and colorimetric.

الطرق الكمية لتقدير محتويات حصى الكلى لدى المرضى باستخدام التقنيات الطيفيه

علي مؤيد عبد الواحد حسين حسن خرنوب حسن احمد حسن

الخلاصة

في هذا البحث تم تقدير المكونات الكيمائية (ايونات الكالسيوم والمغنسيوم والفسفور اللاعضوي) لحصى الكلى باستخدام الطريقه الكمية. تم فحص 43 حصى (14 حصى من الاناث بنسبة 32.6 % و 29 حصى من الذكورو بنسبة 67.4%) باستخدام مطيافية الضوء المرئي عند اطوال موجية مختلفة .الطريقه التحليلية الكمية التي تم استخدامها لتقدير تراكيز هذه الايونات كانت ذات دقة موثوقة وحساسية مع مدى خطي يتراوح بين (5-65)، (0.5-0.05)،و(13.5-1.5) مايكروغرام /مل وبمدى انحراف قياسي(0.004596) و (0.002390) و(0.000756) ونقطة حد الكشف كانت (0.1120) و(0.0177) و (0.1890) مايكروغرام/مل بينما الانحراف القياسي النسبي كان (1.40%)و(2.36%) و (5.04%) على التوالي .ومعظم حصى الكلى وجدت اما صلبة او ناعمة وبأشكال والوان مختلفة. هظمت الحصى بثلاثة محاليل اثنان من حامض النتريك عيارية (1) و (16.5) والثالث عبارة عن الماء الخالي من الايونات حيث وجد اعلى تركيز للكلسيوم والمغنيسيوم والفسفور عند محلول الهضم بحامض النتريك عيارية 16.5.

الكلمات الافتتاحية : حصى الكلى ، الجهاز البولي ، الطرق الكمية ، وقياس المطافية اللونية

Introduction

Kidney stones are also called nephrolithiasis or urolithiasis, they are aggregation of materials or minerals and develop form a small stone or small crystals (crystalluria) in the kidney, urethra or bladder [(1)].Renal calculi also can be defined as the consequence of a variation in conditions of normal crystallization of urine in urinary system. In a healthy Peoples crystals do not form or are so small they are Extraction uneventfully (asymptomatic crystalluria) during urine passage in urinary tract. The rate of crystal nucleation is growth. Normal urine crystallization conditions change and may become a large crystals then cannot be easily eliminated according to the size. In some cases, change urinary conditions affecting crystallization are related to some diseases such as hyperparathyroidism and hypercalciuria[(2)]. Crystalluria becomes aggregation and then becomes stone when the urine becomes highly concentrated .In normal conditions crystalluria pass through the urinary tract without problems. Sometimes, if crystalluria become large enough, they may cause obstruction of the kidney drainage system which may result in severe pain, bleeding, infection or kidney failure. The obstruction sites of stone in the upper urinary system are located at the:

1- Junction where the kidney meets the upper urethra.
2- Mid portion of the urethra.
3- Lower urethra at its entry into the bladder [(3)].

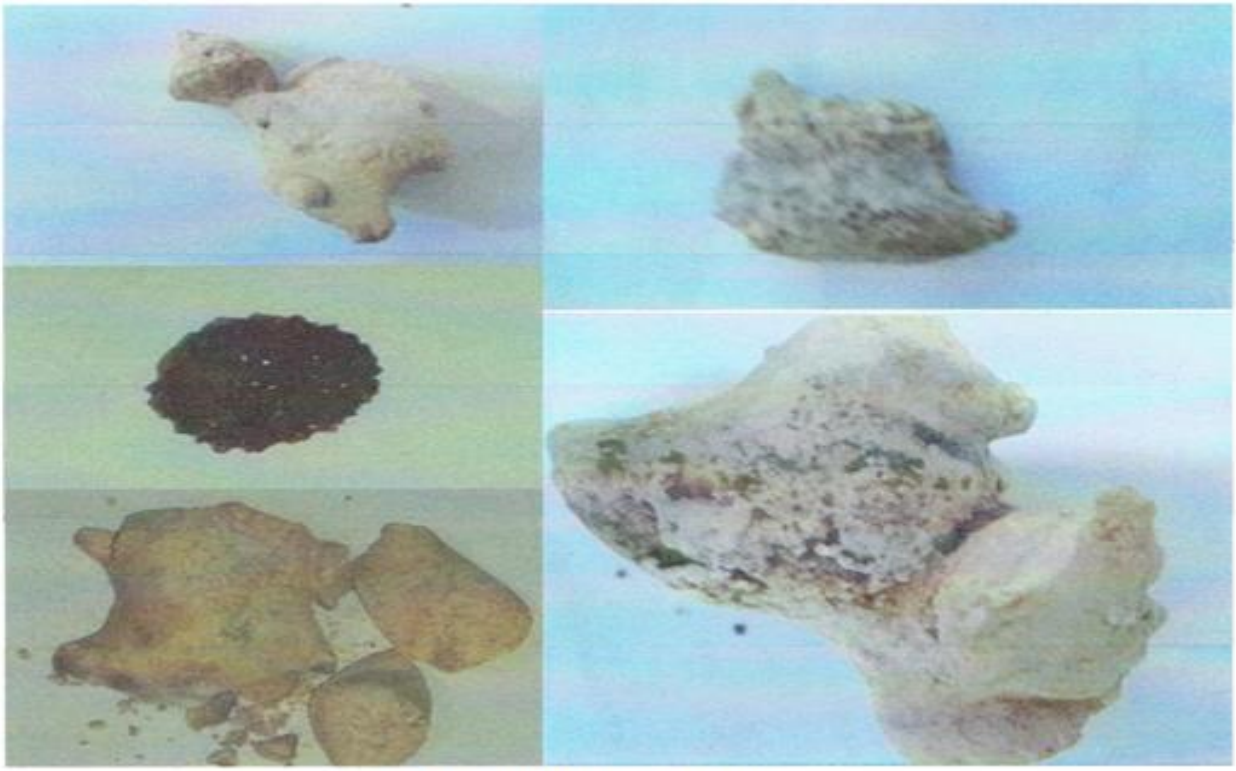
Renal calculi also can be defined as a solid piece of material that forms in a kidney or other sites of urinary system when substances found in the urine become highly concentrated[(4)]. Risk factors responsible for contributing to stone formation have been identified, including environmental ,metabolic, dietary, racial, gender, obstructive uropathology and urinary tract infection[(5)].Bacteria of urinary tract infections (UTI) play an important role in the synthesis of renal stone[(6)].Renal stones are discover about 7000 years ago and maybe earlier. The earliest recorded example is bladder and kidney stones detected in Egyptian mummies dating to 4800 years B.C. (a urinary stone belonging to a 16-year-old boy), urinary stone was found in a boy from 3000 years ago in America[(7)].The existence of kidney stones has been recorded since the beginning of civilization, and lithotomic for the removal of stones is one of the earliest known surgical procedures[(8)].There are several types of kidney stones according to the type of crystals and compositions of which they consist. The majority are calcium oxalate stones, followed by calcium phosphate stones and uric acid stones. More rarely, struvite stones are produced by urea-splitting bacteria in people with urinary tract infections, and people with certain metabolic abnormalities may produce cystine stones [(9)]. Calcium salts, uric acid, cystine, and struvite ($MgNH_4Po_4$) are the basic constituents of most kidney stones in the western hemisphere. Calcium oxalate and calcium phosphate stones make up 85% of the total stones and may be Located in the same stone [(10)].

Materials and Methods

Samples

Forty three of stones (14 from female percentage 32.6% and 29 of male percentage 67.4%) were collected from Anbar teaching hospital. They were recruited from September 2013 until March 2014. Samples were collected from surgeries and laparoscopic operations in Urology Department in Ramadi Teaching

Hospital and others of Anbar hospitals. After stone collected were cleaned by distilled water and let it to dry then kept in plastic cup at room temperature and labeled to be used for qualitative and quantitative analysis .Information of patients and shape of stones listed in fig(1) and table(1).



Fig(1): picture of different stones

Reagents

1N HNO_3, 16.5N HNO_3, and deionized water

Instruments

UV/visible spectrophotometer (mode l160) shimadzu/Japan with double beam.

Quantitative determination of calcium by visible spectrophotometry:

0.01 gm of powder was digested in 1 ml of 1N HNO_3, 1ml of 16.5N HNO_3, and 1ml of deionized water. The concentration of calcium was determined in different digest solution applying spectrophotometric method using o-cresolphthalein complexone which yields a violet colored complex measured at 570 nm. Interference due to Mg^{+2} ions is eliminated by 8-hydroxyquinoline [11,12]. Calibration curve for calcium was prepared using the same spectrophotometric method (fig2).To obtain the concentration of calcium in µg/gm the following relationship was used. The results are shown in table (2)

Concentration of calcium= $\frac{concentration\ in \frac{\mu g}{ml} \ x\ volume\ in\ ml}{weight\ in\ gm}$

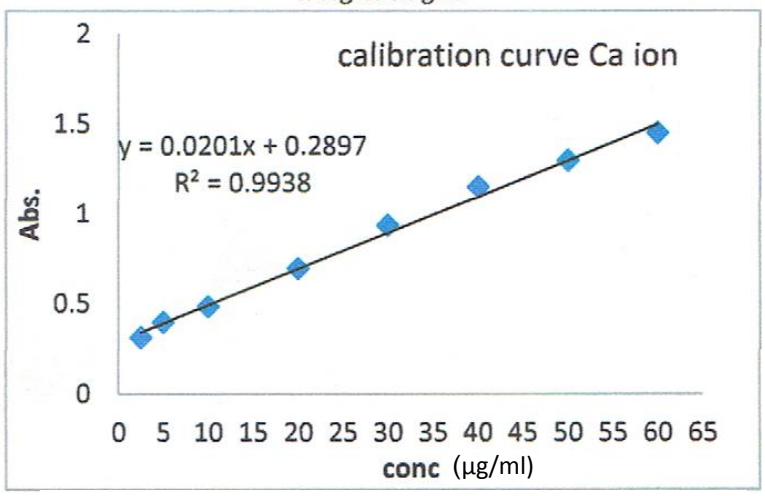


Fig (2):- Calibration Curve of Ca ion

Quantitative determination of magnesium by visible spectrophotometry

0.01gm of powder was digested in 1 ml of 1N HNO_3, 1ml 16.5N HNO_3, and 1mldeionized water. The concentration of magnesium was determined in different digest solution using spectrophotometric method. The method based on the binding of calmagite which is a metallochromic indicator with magnesium at alkaline pH with absorption wavelength 510-550 nm of the complex [13]. The intensity of the chromophore formed is proportional to the concentration of magnesium. Calibration curve for magnesium was prepared using the same spectrophotometric method (fig3). To obtain the concentration of magnesium in µg/gm the same law of calculation in the previous method was used and the results are shown in table (3)

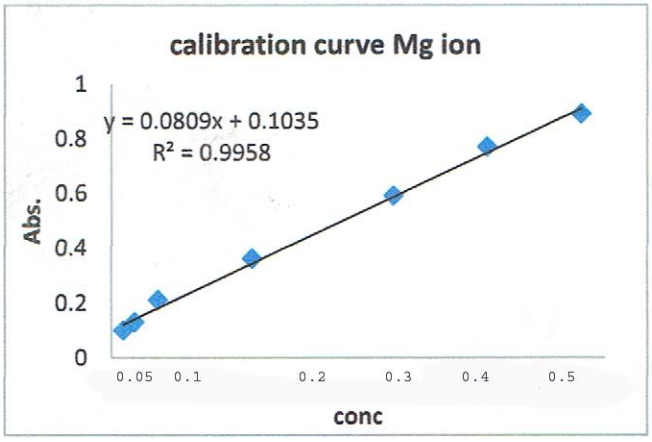


Fig (3):- Calibration curve of Mg ion

Quantitative determination of phosphorus by visible spectrophotometry:

0.01 gm of powder was digested in 1 ml of 1N HNO_3, 16.5N HNO_3, and 1ml deionized water. The concentration of phosphorus was determined in different digest solution using spectrophotometric method. In which inorganic phosphate reacts with molybdic acid to form a phosphomolybdic acid complex [14], and then reduced by ammonium iron (ll)sulphate to molybdenum blue, which measured at 690nm[15,16]. Calibration curve for phosphorus was prepared using the same spectrophotometric method (fig4). To obtain the concentration of phosphorus in µg/gm the same law of calculations in the previous relationship was used and the results are shown in table (4).

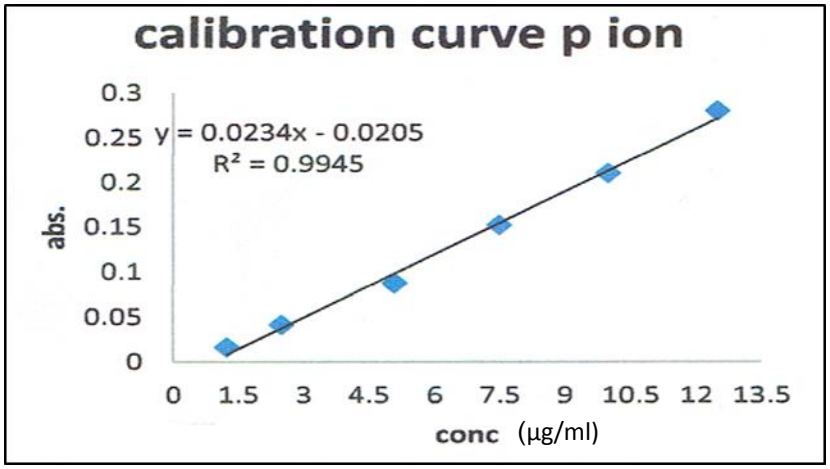


Fig (4):- Calibration curve of P ion

Table (1): Data for Patients and Kidney Stones

Pat. No.	Age /year	sex	History of patient	Weight of Stone /gm	Color of Stone	rigidity
1	65	Male	1 kidney only +stone former	21.21	Yellowish brown	Rigid
2	35	Male	No History	3.3	Dark brown red	Rigid
3	60	Male	No History	9.5	Brown orange	Rigid
4	60	Male	D.M + stone former	20.03	Gray yellow	Rigid
5	51	Male	stone former	0.32	Black	Soft
6	73	Male	D.M+H.T+MI	7.4	White yellow	Soft
7	41	Male	stone former	2.64	black yellow	Rigid
8	25	Male	stone former	1.97	orange yellow	Soft
9	30	Male	stone former	1.27	Orange yellow	Soft
10	40	Female	D.M+HT	0.95	yellow	Soft
11	40	Male	No History	0.59	Black brown	Soft
12	70	Male	No History	12.45	yellow	Rigid
13	60	Female	D.M+ Obesity	10.81	Black yellow	Rigid
14	40	Female	No History	0.86	Brown yellow	Soft
15	23	Male	No History	0.78	Brown yellow	Rigid
16	28	Male	No History	0.54	Brown yellow	Soft
17	70	Female	No History	2.15	Dark brown	Rigid
18	38	Male	No History	0.48	yellow	Soft
19	35	Male	No History	5.56	Black brown	Rigid
20	27	Female	D.M+HT	2.48	Black brown	Rigid
21	50	Female	No History	1.11	Gray yellow	Rigid
22	60	Male	D.M	14.08	Black brown	Rigid
23	43	Male	No History	6.76	Brown yellow	Soft
24	25	Female	No History	0.56	Brown	Rigid
25	23	Female	No History	0.8	Black brown	Rigid
26	33	Male	No History	0.9	Brown yellow	Rigid
27	28	Female	No History	1.5	Brown yellow	Soft
28	40	Female	D.M	0.1	Brown yellow	Soft
29	30	Male	No History	0.2	Brown	Soft
30	27	Male	stone former	1.54	Black	Soft
31	40	Male	D.M	2.7	Black	Rigid
32	35	Male	No History	0.14	White	Soft
33	28	Male	No History	0.10	Black	Soft
34	3	Female	No History	2.10	Brown	Rigid
35	33	Male	H.T	7.13	Dark brown	Rigid
36	3	Female	No History	7.34	Brown	Rigid
37	40	Female	D.M+HT	56.96	Yellowish white	Rigid
38	38	Male	stone former	36.86	Brownish yellow	Rigid
39	28	Male	No History	0.28	Gray	Soft
40	50	Male	D.M	1.69	Black	Soft
41	52	Female	No History	1.71	Yellow	Soft
42	49	Male	stone former	1.99	Gray	Soft
43	29	Male	No History	0.11	Brown	Soft

Table (2): Concentration of Calcium in the Kidney Stones

Stone No.	Visible technique					
	1N HNO_3 mg/dl	Conc. µg/gm	16.5N HNO_3 mg/dl	Conc. µg/gm	D.I.W* mg/dl	Conc. µg/gm
1	7.2	72	15.0	150	4.96	49.6
2	24	240	53.8	538	15.23	152.3
3	22.2	222	28.3	283	10.89	108.9
4	22.92	229.2	29.6	296	17.40	174
5	30.12	301.2	58.4	584	19.30	193
6	11.7	117	18.0	180	10.6	106
7	28.98	289.8	36.6	366	17.7	177
8	24.3	243	28.4	284	17.14	171.4
9	17.1	171	22.0	220	10.5	105
10	23.58	235.8	29.0	290	12.14	121.4
11	29.1	291	40.1	401	17.1	171
12	9.41	94.1	13.2	132	8.7	87
13	28.2	282	42.6	426	17.3	173
14	28.98	289.8	48.5	485	18.96	189.6
15	29.1	29.1	38.2	382	15.6	156
16	30.24	302.4	53.8	538	20.9	209
17	29.04	290.4	52.4	524	21.3	213
18	26.64	266.4	28.2	282	18.71	187.1
19	35.59	355.9	38.8	388	15.66	156.6
20	7.32	73.2	10.0	100	5.75	57.5
21	48.5	485	53.4	534	27.5	275
22	28.8	288	32.8	328	8.83	88.3
23	48.7	487	50.2	502	20.2	202
24	49.7	497	53.4	534	30.6	306
25	48.7	487	51.4	514	10.4	104
26	28.99	289.9	29.8	298	19.9	199
27	34.5	345	40.2	402	18.0	180
28	27.73	277.3	40.3	403	15.4	154
29	11.88	118.8	12.84	128.4	5.3	53
30	40.0	400	45.0	450	16.4	164
31	42.3	423	44.22	442.2	16.995	169.95
32	43.5	435	44.22	442.2	32.64	326.4
33	40.3	403	42.11	421.1	12.12	121.2
34	40.96	409.6	41.325	413.25	9.96	99.6
35	32.46	324.6	39.15	391.5	17.34	173.4
36	6.09	60.9	8.07	80.7	5.64	56.4
37	40.1	401	42.1	421	36.94	369.4
38	27.2	272	28.46	284.6	11.94	119.6
39	24.87	248.7	27.47	274.7	14.4	144
40	32.52	325.2	41.1	411	12.375	123.75
41	19.1	191	20.59	205.9	10.2	102
42	10.8	108	12.46	124.6	8.94	89.4
43	42.39	423.9	44.82	448.2	20.75	207.5

Table (3): Concentration of Magnesium in the Kidney Stones

Stone No.	Visible technique					
	1N HNO_3 mg/dl	Conc. µg/gm	16.5N HNO_3 mg/dl	Conc. µg/gm	D.I.W* mg/dl	Conc. µg/gm
1	1.253	12.53	1.795	17.95	0.876	8.76
2	1.024	10.24	1.740	17.4	0.930	0.93
3	1.296	12.96	2.702	27.02	0.932	9.32
4	0.566	5.66	1.806	18.06	0.627	6.27
5	1.923	19.23	3.597	35.97	1.001	10.01
6	0.549	5.49	1.608	16.08	0.412	0.42
7	1.204	12.04	2.696	26.96	0.798	7.98
8	2.236	22.36	3.580	35.8	1.033	10.33
9	1.696	16.96	2.570	25.7	0.924	9.24
10	3.848	38.48	4.580	45.8	2.091	20.91
11	4.213	42.13	6.558	65.58	3.667	36.67
12	3.593	35.93	5.580	55.8	2.101	21.01
13	0.474	4.74	1.610	16.1	0.420	0.42
14	1.317	13.17	2.380	23.8	0.810	8.1
15	3.543	35.43	4.114	41.14	2.350	23.5
16	2.491	24.91	3.371	33.71	1.240	12.4
17	2.375	23.75	3.580	35.8	0.932	9.32
18	2.333	23.33	3.437	34.37	0.830	8.3
19	4.992	49.92	5.410	54.1	2.246	22.46
20	0.680	6.8	1.410	14.1	0.821	0.8
21	3.092	30.92	4.443	44.43	2.111	21.11
22	0.646	6.46	1.415	14.15	0.211	2.11
23	5.952	59.52	6.580	65.8	3.180	31.8
24	2.073	20.73	3.289	32.89	1.380	13.8
25	3.700	37	4.349	43.49	2.360	23.6
26	0.854	8.54	1.349	13.49	0.440	1.4
27	0.798	7.98	1.415	15.15	0.864	1.64
28	0.302	3.02	1.784	17.84	0.762	1.62
29	0.562	5.62	1.410	14.1	0.370	1.7
30	0.578	5.78	1.460	14.6	0.300	0.3
31	1.962	19.62	2.844	28.44	1.296	12.96
32	2.400	24	4.995	49.95	1.227	12.27
33	0.938	9.38	1.964	19.64	0.616	6.16
34	2.700	27	3.000	30	1.708	17.08
35	0.560	5.6	2.012	20.12	0.426	4.26
36	0.560	5.6	1.892	18.92	0.410	4.1
37	4.41	44.1	5.982	59.82	3.576	35.76
38	0.732	7.32	1.978	19.78	0.518	5.18
39	0.726	7.26	1.994	19.94	0.514	5.14
40	5.154	51.54	5.980	59.8	4.068	40.68
41	0.678	6.78	2.000	20	0.354	3.54
42	0.654	6.54	1.984	19.84	0.354	3.54
43	4.614	46.14	5.286	52.86	3.570	35.7

Table (4): Concentration of Phosphorus in the Kidney Stones

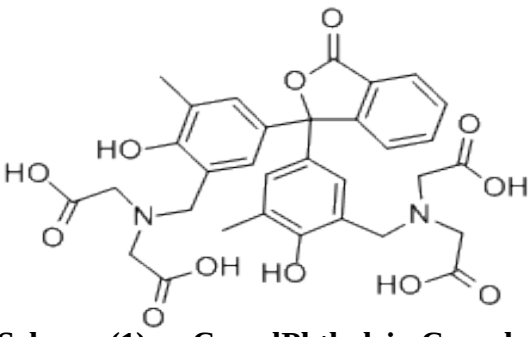
Stone No.	Visible technique					
	1N HNO_3 mg/dl	Conc. µg/gm	16.5N HNO_3 mg/dl	Conc. µg/gm	D.I.W* mg/dl	Conc. µg/gm
1	0.221	2.21	0.336	3.36	0.140	1.4
2	0.162	1.62	0.492	4.92	0.151	1.51
3	0.882	8.82	1.408	14.08	0.173	1.73
4	1.386	13.86	1.876	18.76	0.828	8.28
5	6.840	68.4	8.780	87.8	2.050	20.5
6	1.494	14.94	1.780	17.8	0.915	9.15
7	2.430	24.3	2.516	25.16	2.020	20.2
8	1.008	10.08	1.464	14.64	0.821	8.21
9	0.666	6.66	1.465	14.65	0.180	1.8
10	0.558	5.58	1.486	14.86	0.178	1.78
11	1.548	15.48	1.884	18.84	0.784	7.84
12	1.476	14.76	1.844	18.44	0.860	8.6
13	1.548	15.48	1.868	18.68	1.001	10.01
14	1.404	14.04	1.624	16.24	0.987	9.87
15	0.912	9.12	1.624	16.24	0.323	3.23
16	1.674	16.74	2.660	26.6	1.092	10.92
17	1.404	14.04	1.480	14.8	0.892	8.92
18	1.368	13.68	1.528	15.28	0.632	6.32
19	0.264	2.64	1.344	13.44	0.024	0.24
20	0.360	3.6	0.768	7.68	0.146	1.46
21	0.258	2.58	0.300	3	0.021	0.21
22	0.174	1.74	0.284	2.84	0.011	0.11
23	5.802	58.02	8.600	86	3.546	35.46
24	1.878	18.78	1.400	14	0.996	9.96
25	0.378	3.78	0.585	5.85	0.121	1.21
26	0.156	1.56	0.384	3.84	0.025	0.25
27	0.992	9.92	1.824	18.24	0.667	6.67
28	0.120	1.2	0.366	3.66	0.024	0.24
29	0.126	1.26	0.180	1.8	0.024	0.24
30	0.198	1.98	0.216	2.16	0.013	0.13
31	0.348	3.48	0.394	3.94	0.120	1.2
32	0.324	3.24	0.396	3.96	0.168	1.68
33	0.150	1.5	0.192	1.92	0.130	1.3
34	0.468	4.68	0.504	5.04	0.252	2.52
35	0.276	2.76	0.312	3.12	0.204	2.04
36	0.138	1.38	0.426	4.26	0.120	1.2
37	5.250	52.5	5.490	54.9	3.318	33.18
38	1.662	16.62	2.118	21.18	1.044	10.44
39	0.438	4.38	0.462	4.62	0.402	4.02
40	0.354	3.54	0.462	4.62	0.288	2.88
41	0.234	2.34	0.306	3.06	0.168	1.68
42	0.384	3.84	0.534	5.34	0.366	3.66
43	0.270	2.7	0.318	3.18	0.234	2.34

* D.I.W: deionized water

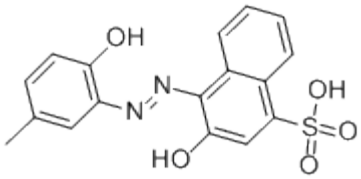
Results and Discussion

In the current study table (1) gives the shape of stones showed in fig (1) which are mulberry stone, Jack stone, staghorn stone and other different shapes. The stones are different in color, dark in patients while pale in others. From data in table (1) the range of age between (23-73years) and only two cases were 3 years. Males always have higher weight of stone than females. The first cause of higher weight of stone in male is the nature of diet and the environmental factor. Stone with calcium and magnesium was more rigid than other stones. From patient's information there are 24 patients didn't have pathological history while 11 patients were under diabetic mellitus. Tables (2,3, and4) show 40 stones(93.0%) were content calcium while 3 stones (7.0%) without calcium. Magnesium appeared in 10 stones (23.3%) and 33 stones without magnesium have percentage 76.7%. Patients with phosphorus were 16.3% while 83.7% of patients didn't have it. The experimental work show the calcium determination is based on the reaction of calcium with o-Cresolphthalein Complexone (scheme 1) that is to form a Ca^{+2}- o- Cresolphthalein complex with a violet color and by which the absorbance is measured , while the role of 8-hydroxyquinoline (metal chelator) is to remove the magnesium ion from the solution by precipitated as a bis[8-hydroxyquinoline]magnesium(II) complex to avoid the interference with calcium ion measurement as shown in (scheme2) . Calmagite (scheme3) is a reagent for quantitative determination of

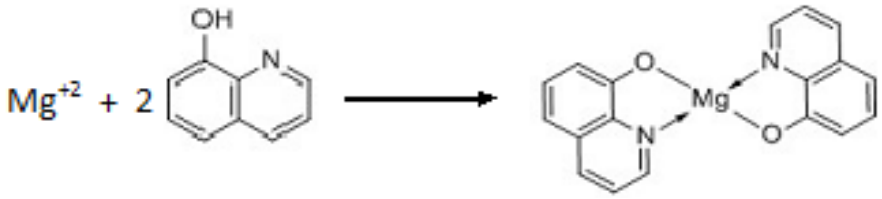
magnesium in the sample forms a red colored complex with the magnesium in this sample and the intensity of the color formed is directly proportional to the concentration of magnesium in the sample .Molybdenum blue formed in the determination of phosphorus is proportional to the amount of phosphorus present in the sample which is measured by the absorbance. Tables (2,3,and 4)show that 16.5N of digest solution was the best solution for releasing the compositions of stones more than other digestion solutions, while deionized water was slight low to release the compositions . The analytical quantitative methods used for determination the concentration of calcium, magnesium, and phosphorus ions were reliable and sensitive with standard deviation 0.004596, 0.002390, and 0.000756 respectively. Lower detection limit (L.O.D.) were 0.1120, 0.0177, and 0.189 mg/dl while the (RSD) were 1.4%, 2.36%, and 5.04 % for standard solutions of calcium, magnesium, and phosphorus ions respectively.Finally, the reliable analysis of different kidney stones could definitely be helpful in the determination quantitatively the concentration of these ions . These chemical analysis methods are simple, fast, and precise.



Scheme (1): o-CresolPhthalein Complexone



Scheme (3): Calmagite



Scheme (2): Suggested reaction of Mg^{+2} with 8-hydroxyquinoline to form Bis [8-hydroxyquinoline] magnesium (II) 2:1 complex

References

1. Smith J, Mattoo TK, Stapleton FB. Patient information: Kidney Stones in children, (2010).

2. Corbetta S, Baccarelli A, Aroldi A, Vicentini L, Fogazzi GB, Eller-Vainicher C, Ponticelli C, Beck-Peccoz P, Spada A: Risk factors associated to kidney stones in primary hyperparathyroidism. J.Endocrinol Invest. (2005); 28:122-128.

3. Kidney Stone Clinic Dr. Raymond Koidney Stone Clinic Nepean, Westmead, and Macquarie Street www.stoneclinic.com.au Ph: 02 47 21 8383 Page 4 of 4 (Urology), (2009).

4. Urinary tract stones. In: Litwin MD, Saigal CS, eds. Urologic Diseases in America. Department of Health and Human Services, Public Health Service, National Institutes of Health, National Institute of Diabetes and Digestive and Kidney Diseases. Washington, D.C.: Government Printing Office. NIH publication 12–7865,(2012).

5. Calvert RC, Burgess NA. Urolithiasis and obesity: metabolic and technical considerations. CurropinUrol.(2005) ;15(2):113-7.

6. Jan H, Akbar I, Kamran H, Khan J. Frequency of renal stone disease in patients with urinary tract infection. J .Ayub Med Coll Abbott bad.(2008);20(1):60-2.

7. Menon, M., Parulkar, B.G., and Drach, G.W. Urinary lithiasis: etiology, diagnosis and medical management. In Campbell's Urology. Walsh, P.C., Retick, A.B., Stamey, T.A., and Vaughan, E.D., Eds. W.B. Saunders, Philadelphia, pp. 2661–2670, (1998).

8. Potts, Jeannette M. Essential Urology: A Guide to Clinical Practice. Humana Press. pp.129.(2004).

9. Collins, C. Edward A Short Course in Medical Terminology. Lippincott Williams & Wilkins. (2005).

10. John R. Aspin :Harrison's Principles of Internal Medicine .Electronic version 15th Edition. P. 283-402. (2001).

11. Daud.M.Biotechnologist ,p,8, 11, (1994).

12. Cowley M.D determination of calcium, (1986).

13- Connetry H.V. and ybiggs, A.R. Am.J.Clin. Path. (1966);45:290.

14. Taussky H.A. J. boil. Chem.(1953); 202:675.

15. Goldenberg H.C. and Clin. Chem. :12:871,(1966).

16. Clinical Chemistry principles and technique 2nd Edition (1974) by Michale Marrshal.