Identification of Groundwater Components in Western Area of Kingdom of Saudi Arabia Using Raman Spectroscopy

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Abstract: The aim of this study is to identify the components of water wells in the western region of Saudi Arabia, using Raman spectroscopy. Water wells samples were collected from different areas, distances apart, and same in the depths. The samples were analyzed by LIRA 300 Raman spectrometer. The results showed that the samples contain different materials, beside the water, with different amounts; like: acids, aromatic molecules, salts, amides, alkynes, phenol, ester and sulfonamide.

Keywords: Raman Spectroscopy, Water Characterization, Groundwater in Madina

1. Introduction

Water is one of the controlling factors for biodiversity and the distribution of Earth's varied ecosystems, communities of animals, plants, and bacteria and their interrelated physical and chemical environments [1]. Water is the most abundant and common fluid existing in nature. In spite of its apparent structural simplicity, it presents some unusual peculiarities, totally dominated by hydrogen bonding, that makes it possibly the most complex of all molecular liquids. Owing to its nonlinear bent structure, water makes several forms of crystal in the solid state and leads to a fluctuating hydrogen bond network in the liquid one. It plays a fundamental role in many natural processes where it is confined or is contact with substrates, involving different fields from geology, biology, chemical engineering and the sustaining of life itself. Vibrational spectroscopy is a powerful tool for studying water structure and dynamics, both in the bulk and confined state, as the spectra are sensitive to local environment of the molecule. In particular, Raman spectroscopy is one of the most employed techniques to study solid and liquid H2O since it provides direct information on inter- and intra-molecular vibrational modes [2]. Surface and ground water are main sources of drinking water. Particularly, ground water stored in aquifers makes up around 90% of potable water worldwide and is the largest reservoir of fresh water on the earth [3].

Water wells are the main sources of water used, and around this importance has many studies to determine the components and identify them in a clear manner. Raman spectroscopy is one of the techniques that can be used to monitor the molecular vibrations of the water components and identify them precisely.

Principles of Raman spectroscopy

The Raman effect is the phenomenon of a change of frequency of light when it is scattered by polyatomic molecules. This phenomenon may only happen if some energy is exchanged between the incoming photon and the scattering molecule. Antistokes and Stokes Raman correspond to the cases when the photon gains or losses energy, respectively, upon interaction with the molecules [4].

For many years Raman spectroscopy has been a powerful tool for the investigation of molecular vibrations and rotations. In the pre-laser era, however, its main drawback was a lack of sufficiently intense radiation sources. The introduction of lasers, therefore, has indeed revolutionized this classical field of spectroscopy. Lasers have not only greatly enhanced the sensitivity of spontaneous Raman spectroscopy but they have furthermore initiated new spectroscopic techniques, based on the stimulated Raman effect., such as coherent anti-Stokes Raman scattering (CARS) or hyper-Raman spectroscopy [5].

Vibrational spectroscopy refers to the measurement of the

vibrational energy levels in a molecule which are associated with its chemical bonds. The vibrational spectrum is rich in chemical composition information of the sample, so it has been applied for chemical analysis, such as water quality, material science and probing physical states [6].

The aim of Raman spectroscopy experiments is to probe the molecular vibrations, probing the transition between the ground state and the excited vibrational states. The transitions are observed as bands in the vibrational spectrum. Each molecule has a specific set of vibrational bands, which are defined by their frequencies, shapes, and intensities. By analyzing these properties, it is possible to get information about the local coordination of the atoms in the material. The intensity of the each band is proportional to the concentration and to the scattering cross-section of the vibrating units [7].

2. The Experimental Part

To record the Raman spectra of the samples a Laser Raman spectrometer model LIRA-300 was used. The light source of this spectrometer is a diode pumped solid state laser with wavelength of 532 nm and output power of 40 mW. The data were collected and shown by the spectrometer as spectra.

Four water samples were collected from ground wells in Madina in the western region of Saudi Arabia. Each sample was put it in the sample cell of the spectrometer by injection of 1mL of water in the cell and Raman spectrum was recorded in the region from 0 to 4000 cm-1. The Raman shift, in wavenumber, and the change in intensities of the scattered light in Raman spectra were compared with data in the references and previous studies.

3. Results and Discussion

Figure (1) shows the Raman spectrum of a sample taken from a well in the area of Madina Alarak in the range from 1003.4 to 3782.0 cm^{-1}. It shows clear peaks and by comparison with the results recorded in some references, we found that these peaks are belong to the vibrations of water molecules and some other materials as listed in Table (1).
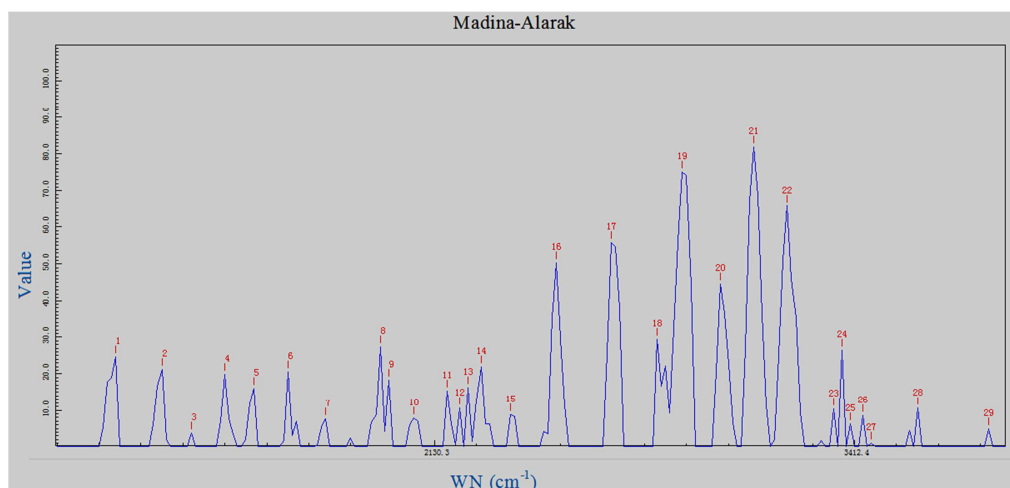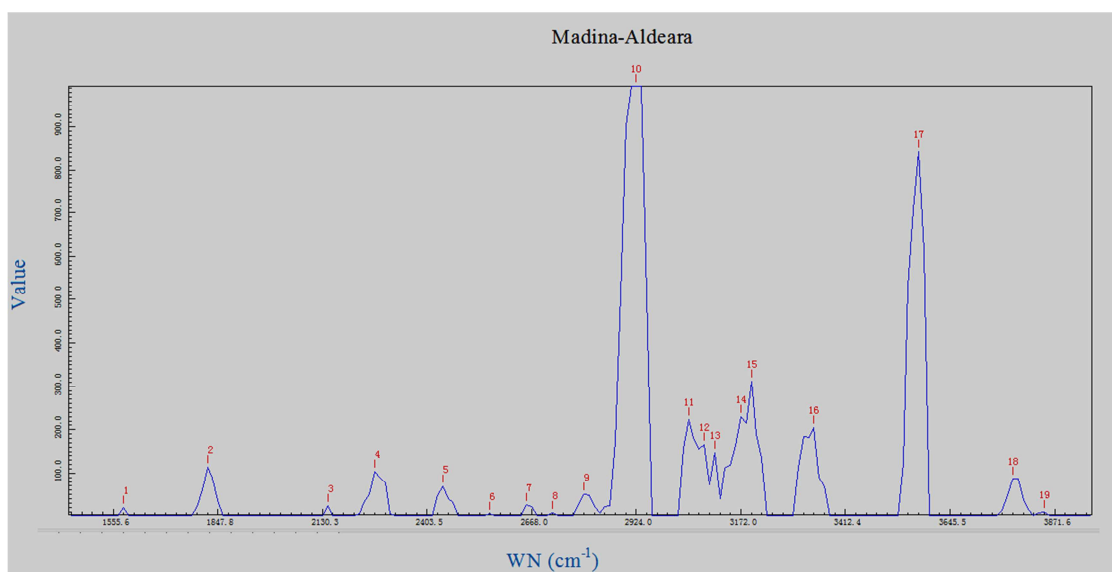

Figure 1. Raman spectrum of ground well water sample collected from (Madina Alarak) in the range from 1003.4 to 3782.0 cm^{-1}.

Table 1. The wave number, intensities, and Functional Group/ Vibration of peaks in the Raman spectra of the ground water sample collected from Madina Alarak.

No. of Peak	Wavenumber (cm^{-1})	Functional Group/ Vibration	Intensity
1	1003.4	Aromatic rings	24.615
2	1175.8	Sulfonamide	21.195
3	1283.9	-	3.690
4	1405.7	CH$_2$, CH$_3$	19.800
5	1510.9	-	16.065
6	1629.6	C = C	20.520
7	1761.2	Lactone	7.695
8	1947.8	-	27.405
9	1976.1	-	18.315
10	2060.6	Isothiocyanate	7.920
11	2171.9	Alkyne	15.300
12	2213.2	Aromatic Nitrile	10.575
13	2240.7	Nitrile	16.290
14	2281.7	-	21.825
15	2376.6	P – H	8.820
16	2523.6	-	50.220
17	2693.9	Aldehyde	55.755
18	2835.3	O – CH$_3$	29.385

No. of Peak	Wavenumber (cm^{-1})	Functional Group/ Vibration	Intensity
19	2911.4	C – CH$_3$	74.970
20	3024.1	= CH$_2$	44.595
21	3123.0	OH	81.855
22	3220.7	Alcohol	65.700
23	3353.0	-	10.350
24	3376.8	Phenol	26.415
25	3400.5	Amide, Amine	6.345
26	3436.0	OH	8.640
27	3459.6	OH	1.125
28	3587.9	-	10.620
29	3782.0	-	4.815

Figure (2) shows the Raman spectrum in the range from 1585.3 to 3849.3 cm^{-1} of a water sample taken from a well Aldeara in Madina area which shows clear peaks describe the vibration of water molecules and some components to other materials as illustrated in Table (2)
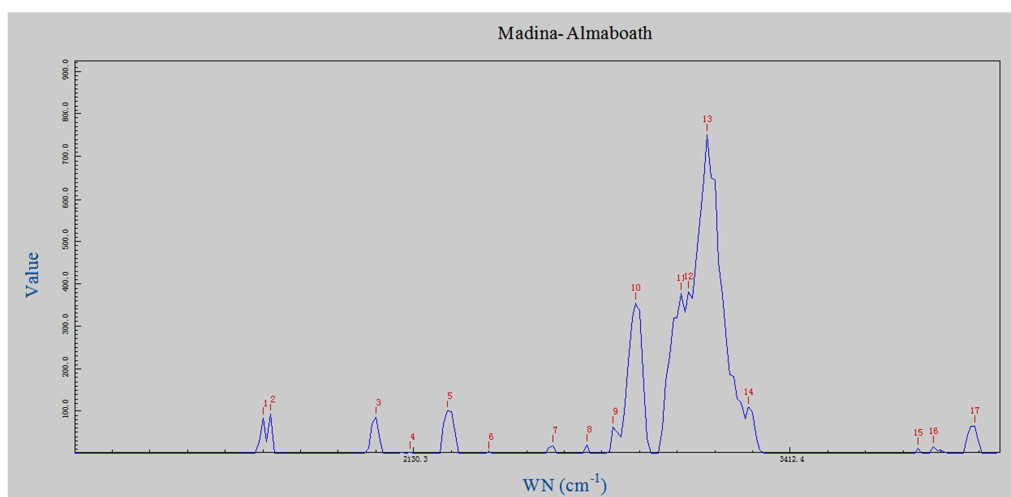

Figure 2. *Raman spectrum of ground water sample collected from (Madina Aldeara) in the range from 1585.3 to 3849.3cm^{-1}.*

Table 2. *The wave number, intensities, and Functional Group/ Vibration of peaks in the Raman spectra of the ground water sample collected from Madina Aldeara.*

No. of Peak	Wavenumber (cm^{-1})	Functional Group/ Vibration	Intensity
1	1585.3	Aliphatic azo	19.980
2	1819.1	Anhydride	113.265
3	2144.2	Azide	24.075
4	2268.1	Diazonium salt	104.130
5	2443.8	-	68.715
6	2563.2	Th iol	4.860
7	2654.9	-	26.550
8	2719.8	Aldehyde	7.155
9	2797.0	N – CH$_3$	50.220
10	2924.0	C – CH$_3$	1232.730
11	3049.0	= CH$_2$	222.930
12	3086.1	Aromatic C – H	164.880
13	3110.7	OH	148.140
14	3172.0	Amide, Amine	229.320
15	3196.4	Amide, Amine	311.850
16	3341.0	Phenol	204.255
17	3576.3	-	842.985
18	3782.0	-	86.850
19	3849.3	-	9.675

In the sample taken from Madina /Almaboath (figure 3) there was a clear picture of the water components and some other materials. Table 3 illustrates the analysis of this spectrum.
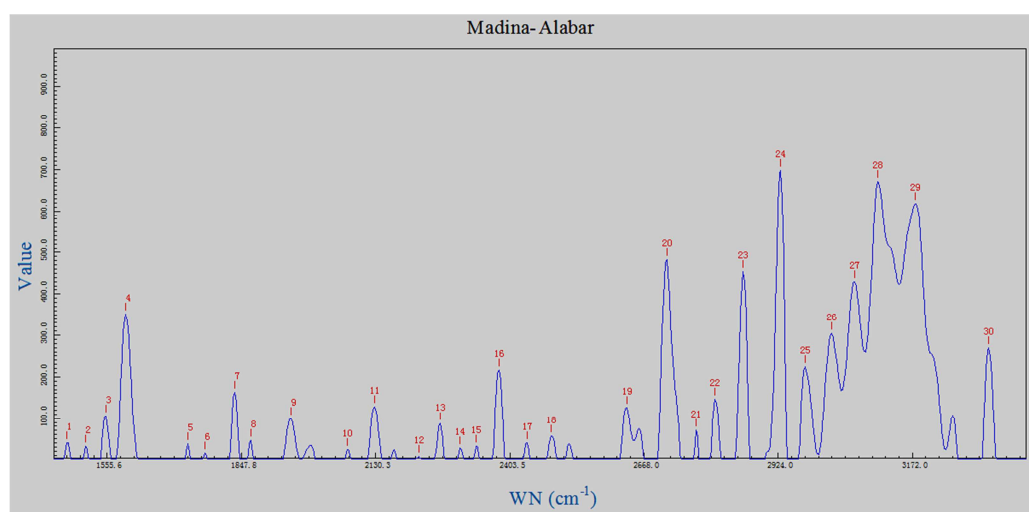
Figure 3. Raman spectrum of ground water sample collected from (Madina Almaboath) in the range from 1555.6 to 3971.2cm^{-1}.

Table 3. The wave number, intensities, and Functional Group/ Vibration of peaks in the Raman spectrum of the ground water sample collected from Madina Almaboath.

No. of Peak	Wavenumber (cm^{-1})	Functional Group/ Vibration	Intensity
1	1555.6	Aliphatic azo	83.160
2	1585.3	Aromatic / Hetro ring	93.240
3	1990.3	-	84.870
4	2116.4	Si – H	3.870
5	2254.4	Diazonium salt	101.295
6	2403.5	P – H	3.240
7	2628.8	-	18.225
8	2745.6	-	19.305
9	2835.3	O – CH$_3$	61.515
10	2911.4	CH$_2$	355.680
11	3061.4	= CH$_2$	377.685
12	3086.1	OH	382.185
13	3147.5	OH	750.690
14	3281.1	Alkyne	109.530
15	3804.5	-	11.880
16	3849.3	-	16.110
17	3971.2	-	64.215

Figure (4) shows the Raman spectrum of the sample collected from a well in the Alabar area in Madina. The vibrations of water molecules are appeared in the spectrum beside some other vibrations. These vibrations were consistent with many previous studies as listed in Table (4).

Figure 4. Raman spectrum in the range from 1466.0 to 3309.9cm^{-1} of ground water sample collected from (Madina Alabar).

Table 4. The wavenumber, intensities, and Functional Group/ Vibration of peaks in the Raman spectrum of the ground water sample collected from Madina Alabar.

No. of Peak	Wavenumber (cm^{-1})	Functional Group/ Vibration	Intensity
1	1466.0	Aromatic ring	40.722
2	1507.9	-	31.190
3	1552.6	Aliphatic azo	105.957
4	1597.1	Nitro	350.549
5	1732.1	Aliphatic ester	37.352
6	1769.9	Lactone	15.852
7	1833.5	-	162.959
8	1867.9	-	46.346
9	1953.5	-	98.864
10	2071.8	Isothiocyanate	23.499
11	2127.5	Azide	128.634
12	2218.7	Aromatic Nitrile	6.263
13	2262.6	Isocyanate	87.734
14	2303.5	$P-H$	28.202
15	2336.1	$P-H$	31.690
16	2382.0	$P-H$	217.010
17	2438.4	-	39.018
18	2486.4	-	56.905
19	2634.1	-	126.117
20	2712.1	Aldehyde	481.873
21	2768.8	$N-CH_3$	71.527
22	2804.7	CH_2	145.896
23	2858.2	$C-CH_3$	453.543
24	2929.0	CH_2	696.694
25	2974.2	Aromatic $C-H$	223.762
26	3024.1	$=CH_2$	303.500
27	3066.3	$=CH_2$	428.811
28	3108.3	OH	670.669
29	3176.9	Amide, Amine	618.755
30	3309.9	Amide, Amine	270.332

Through the analysis of the four samples collected from Madina area it was found that the vibration modes of some materials are appeared in all the samples while other modes are appeared in some samples and disappeared in other samples. That is as follows:

1. Aromatic ring: appeared in the spectra of (Alarak, Alabar) wells, with intensities (24.615, 40.722), respectively.

2. Sulfonamide, CH_2 and CH_3, $C = C$, Alcohol, Nitrile: appeared in the spectra of Alarak well, with intensities (21.195, 19.8, 20.520, 65.7, 16.290), respectively.

3. Isothiocyanate: appeared in the spectra of (Alarak, Alabar) wells, with different intensities (7.920, 23.499), respectively.

4. Alkyne: appeared in the spectra of (Alarak, Almaboath) wells, with different intensities (15.300, 109.530), respectively.

5. Aromatic nitrile: appeared in the spectrum of (Alarak, Alabar) wells, with different intensities (10.575, 6.263), respectively.

6. $P - H$: appeared in the spectra of (Alarak, Almaboath, Alabar) wells, with different intensities (8.820, 3.240, 217.01), respectively.

7. Aldehyed: appeared in the spectra of (Alarak, Aldeara, Alabar) wells, with different intensities (55.755, 7.155, 481.873), respectively.

8. O - CH_3: appeared in the spectra of (Alarak, Almaboath) wells, with different intensities (29.385, 61.515), respectively.

9. C - CH_3: appeared in the spectra of (Alarak, Aldeara, Alabar) wells, with different intensities (74.970, 1232.730, 453.543), respectively.

10. $= CH2$: appeared in the spectra of (Alarak, Aldeara, Almaboath, Alabar) wells, with different intensities (44.959, 222.930, 377.685, 428.811), respectively.

11. OH: appeared in the spectra of (Alarak, Aldeara, Almaboath, Alabar) wells, with different intensities (81.853, 148.140, 750.690, 670.669), respectively.

12. Lactone: appeared in the spectra of (Alarak, Alabar) wells, with different intensities (7.695, 15.852), respectively.

13. Phenol: appeared in the spectra of (Alarak, Aldeara) wells, with different intensities (26.415, 204.255), respectively.

14. Amide, Amine: appeared in the spectra of (Alarak, Aldeara, Alabar) wells, with different intensities (6.345, 311.850, 618.755), respectively.

15. Aliphatic azo: appeared in the spectra of (Aldeara, Almaboath, Alabar) wells, with different intensities (19.980, 83.160, 105.957), respectively.

16. Anhydride, Th iol: appeared in the spectra of Aldeara well, with intensities (113.265, 4.860) respectively.

17. Azide: appeared in the spectra of (Aldeara, Alabar) wells, with different intensities (24.075, 128.634), respectively.

18. Diazonium salt: appeared in the spectra of (Aldeara, Almaboath) wells, with different intensities (104.130101.295), respectively.

19. N - CH_3: appeared in the spectra of (Aldeara, Alabar) wells, with different intensities (50.220, 71.527), respectively.

20. Aromatic C-H: appeared in the spectra of (Aldeara, Alabar) wells, with different intensities (222.930, 223.762), respectively.

21. Aromatic/hetro ring, Si - H: appeared in the spectra of Aldeara well, with intensities (93.240, 3.870), respectively.

22. CH_2: appeared in the spectra of (Aldeara, Alabar) wells, with different intensities (355.680, 696.694), respectively.

23. Aliphatic Ester, Isocyanate, Nitro: appeared in the spectra of Alabar well, with intensities (37.352, 87.734, 350.549), respectively.

4. Conclusions

Raman technique provides precise information about the contents of the ground water wells. Significant differences in the peaks intensities and peaks shift in the spectra of different water samples were recorded. Raman spectroscopy can be utilized for this purpose.

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