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Identification Of Groundwater Components In Western Part 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 close 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 Jeddah

I. 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 H_2O 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.

Five water samples were collected from ground wells in Jeddah and Mecca 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 Jeddah Ajuad in the range from 367.2 to 3763.9 cm^{-1}.

It shows clear peaks and by comparison with the vibrations recorded in some references, we found that these vibrations describe the vibrations of water molecules and some components of other materials as listed in Table 1.

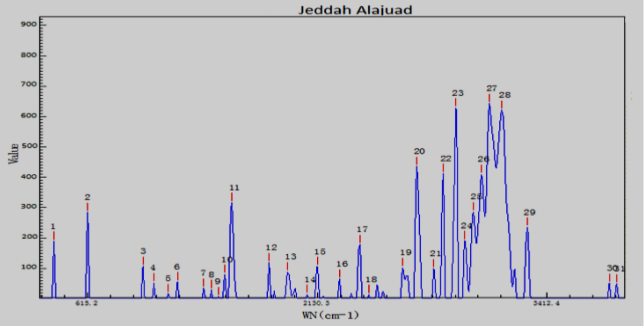

Fig. 1. Raman spectrum of ground well water sample (Jeddah Ajuad) in the range from 367.2 to 3763.9 cm^{-1}.

TABLE 1. The wavenumber, intensities, and Functional Group/ Vibration of peaks in the Raman spectrum of the ground water samples collected from Jeddah Ajuad

Peak no.	Peak Wavenumber (cm^{-1})	Intensity (a. u.)	Functional Group/ Vibration	References
1	367.2	189.424	X metal – O	[8, 9]
2	615.2	284.624	C = S	[8,9]
3	1009.7	107.198	Aromatic ring	[8, 9,10, 11]
4	1079.1	52.731	Si – O – Si	[8, 9]
5	1179.0	17.031	Si – O – C	[8, 9]
6	1240.8	55.625	Sulfonic acid	[8, 9]
7	1411.7	35.136	CH_2 , CH_3	[8, 9, 10]
8	1466.0	30.176	Aromatic ring	[10, 11]
9	1507.9	7.627	C = C	[8, 9, 10]
10	1549.7	80.190	Aliphatic azo	[8, 9]
11	1597.1	316.907	Aromatic/hetero ring	[9, 10, 11]
12	1830.6	119.052	Anhydride	[8, 9]
13	1950.6	88.712	-	-
14	2069.0	14.285	Isothiocyanate	[8, 9]
15	2130.3	106.136	Thiocyanate	[8, 9]
16	2262.6	64.756	Diazonium salt	[8, 9]
17	2382.0	178.422	P – H	[8, 9]
18	2435.7	14.139	-	-
19	2631.5	102.552	-	-
20	2709.5	435.845	Th iol	[8, 9]
21	2802.1	98.926	CH_2	[8, 9, 10]
22	2858.2	412.409	$C – CH_3$	[8, 9]
23	2924.0	628.086	CH_2	[9, 10]
24	2974.2	191.291	Aromatic C – H	[8, 9]
25	3024.1	285.783	$= CH_2$	[9, 10]
26	3063.8	409.052	$= CH_2$	[9, 10]
27	3108.3	642.707	OH	[8, 9]
28	3176.9	620.887	Amide , Amine	[8, 9]
29	3307.5	235.570	Phenol	[8, 9]
30	3727.7	51.026	-	-
31	3763.9	49.233	-	-

Figure 2 shows the Raman spectrum in the range from 974.9 to 3824.7cm^{-1} of a water sample taken from Almazara well in Jeddah area which shows clear peaks describe the vibration of water molecules and some components to other materials as illustrated in Table 2.

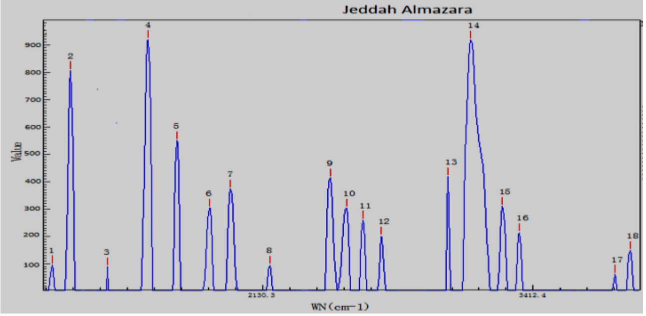

Fig. 2. Raman spectrum of ground water sample (Jeddah Almazara) in the range from 974.9 to 3824.7cm^{-1}.

TABLE 2. The wavenumber, intensities, and Functional Group/ Vibration of peaks in the Raman spectrum of the ground well water samples obtained from Jeddah Almazara

Peak no.	Peak Wavenumber (cm^{-1})	Intensity	Functional Group/ Vibration	References
1	974.9	95.939	Aromatic ring	[9, 10, 11]
2	1082.2	805.765	Si – O – C	[8, 9]
3	1293.1	88.476	-	-
4	1522.9	919.309	C = C	[9, 10, 11]
5	1676.6	549.584	C = C	[8, 9, 10, 11]
6	1850.7	303.524	C = C	[9, 10, 11]
7	1964.8	373.570	-	-
8	2166.4	94.466	Thiocyanate	[8, 9]
9	2470.5	413.683	-	-
10	2550.0	302.806	Thiol	[8, 9]
11	2628.8	258.981	-	-
12	1717.2	200.584	Anhydride	[8, 9]
13	3031.6	418.332	= CH_2	[8, 9, 10]
14	3135.3	917.323	OH	[8, 9]
15	3276.3	309.899	Alkyne	[8, 9]
16	3353.0	213.193	Phenol	[8, 9]
17	3761.0	61.490	-	-
18	3824.7	147.950	-	-

In the sample taken from the well in Jeddah-Alsafa (figure 3) there was a clear picture of the water components and some other materials. Table 3 illustrates the analysis of this spectrum.

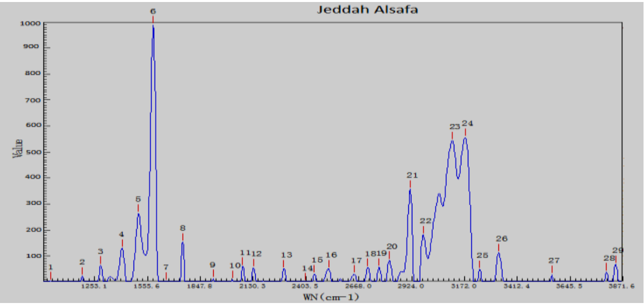

Fig. 3. Raman spectrum of ground water sample collected from (Jeddah-Alsafa)

TABLE 3. The wavenumber, intensities, and Functional Group/ Vibration of peaks in the Raman spectrum of the ground water samples obtained by Raman spectrometer : Jeddah Alsafa

Peak no.	Wavenumber (cm^{-1})	Intensity	Region (cm^{-1})	Functional Group	References
1	993.9	4.346	990 – 1100	Aromatic ring	[8, 9, 10]
2	1182.1	22.715	1120 – 1190	Si – O – C	[8, 9]
3	1290.0	64.370	-	-	-
4	1411.7	130.146	1405 – 1455	CH_2 , CH_3	[8, 9, 10]
5	1504.9	264.395	1450 – 1505	Aromatic ring	[8, 9, 10, 11]
6	1588.3	988.648	1540 – 1590	Aliphatic azo	[8, 9]
7	1662.0	2.684	1630 – 1665	C = N	[8, 9, 10]
8	1752.5	153.282	1735 - 1790	Lactone	[8, 9]
9	1916.5	13.268	-	-	-
10	2121.3	9.363	2020 – 2100	Isothiocyanate	[8, 9]
11	2074.6	60.049	2070 – 2250	Alkyne	[8, 9]
12	2133.1	54.347	2110 – 2160	Azide	[8, 9]
13	2289.9	50.717	-	-	-
14	2398.2	0.267	2290 – 2420	P – H	[8, 9]
15	2446.4	30.645	-	-	-
16	2518.3	50.881	2530 – 2610	Thiol	[8, 9]
17	2644.5	30.298	-	-	-
18	2712.1	55.579	2680 – 2740	Aldehyde	[8, 9]
19	2766.2	56.932	2750 - 2800	N – CH_3	[8, 9]
20	2817.4	83.639	2810 – 2960	C – CH_3	[8, 9]
21	2916.4	357.039	2900 – 2940	CH_2	[8, 9, 10]
22	2979.2	181.612	2870 – 3100	Aromatic C – H	[8, 9, 10]
23	3115.6	543.583	2880 – 3530	OH	[8, 9]
24	3174.4	555.915	3150 – 3480	Amide , Amine	[8, 9]
25	3242.5	48.588	3210 – 3250	Alcohol	[8, 9]
26	3329.1	113.235	3200 – 3400	Phenol	[8, 9]
27	3564.7	28.316	3100 – 3650	O - H	[8, 9, 10]
28	3802.2	38.187	-	-	-
29	3840.4	67.753	-	-	-

Figure (4) shows the Raman spectrum of the sample collected from a well in the omalgoura area in Jeddah. 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.

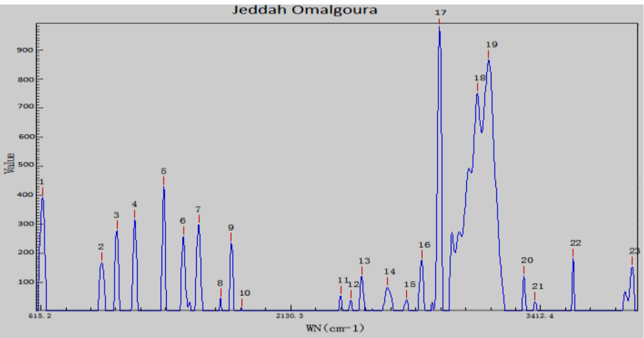

Fig. 4. Raman spectrum in the range from 625.1 to 3833.7 cm^{-1} of ground water collected from (Jeddah Omalgora)

TABLE 4. The wavenumber, intensities, and Functional Group/ Vibration of peaks in the Raman spectrum of the ground water samples collected from Jeddah-Omalgora

Peak No.	Wavenumber (cm^{-1})	Intensity	Functional Group/ Vibration	References
1	625.1	392.974	C = S	[8, 9]
2	1006.6	168.601	Aromatic ring	[8, 9, 10, 11]
3	1104.1	278.486	Sulfonic acid	[8, 9]
4	1216.1	315.769	-	-
5	1393.6	429.605	Si – O – C	[8, 9]
6	1510.9	258.246	C = C	[8, 9, 10, 11]
7	1603.0	298.032	Aromatic/hetero ring	[8, 9, 10, 11]
8	1732.1	44.896	Ester	[8, 9]
9	1793.1	235.723	Anhydride	[8, 9]
10	1853.6	10.128	C = C	[8, 9, 10, 11]
11	2403.5	53.703	P – H	[8, 9]
12	2457.1	39.191	-	-
13	2515.7	120.357	-	-
14	2649.7	83.397	-	-
15	2750.8	39.693	N – CH_3	[8, 9]
16	2827.7	176.172	C – CH_3	[8, 9]
17	2918.9	980.408	CH_2	[8, 9, 10, 11]
18	3105.8	750.901	OH	[8, 9]
19	3162.2	864.619	Amide , Amine	[8, 9]
20	3333.9	121.918	Phenol	[8, 9]
21	3386.3	32.947	Phenol	[8, 9]
22	3564.7	181.847	O – H	[8, 9]
23	3833.7	153.959	-	-

Figure (5) illustrates Raman spectrum of the groundwater collected from (Jeddah shakreen) in the range from 769.2 to 3838.1 **cm**$^{-1}$. Table (5) lists the analysis of this spectrum.

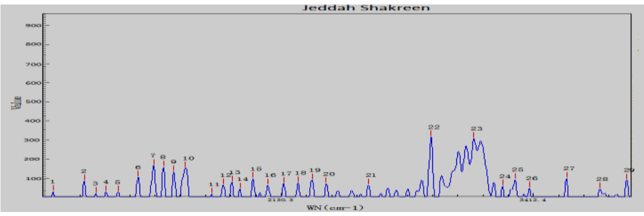

Fig. 5. Raman spectrum of ground water collected from (Jeddah Shakreen)

Table 5. The wavenumber, intensities, and Functional Group/ Vibration of peaks in the Raman spectrum of Jeddah Shakreen sample

Peak No.	Wavenumber (cm^{-1})	Intensity	Functional Group/ Vibration	References
1	769.2	29.575	C - F	[8, 9]
2	968.5	84.328	Aromatic ring	[8, 9, 10, 11]
3	1041.3	19.514	Sulfonic acid	[8, 9]
4	1104.1	28.230	Sulfonamide	[8, 9]
5	1179.0	26.940	Sulfonic acid	[8, 9]
6	1302.2	105.502	CH_2	[8, 9, 10]
7	1396.6	166.729	Aromatic azo	[8, 9]
8	1453.9	157.659	CH_2 , CH_3	[8, 9, 10]
9	1516.9	133.242	C = C	[8, 9, 10, 11]
10	1585.3	152.540	Aromatic/hetero ring	[8, 9, 10, 11]
11	1738.0	16.037	Ester	[8, 9]
12	1804.6	63.829	Anhydride	[8, 9]
13	1853.6	78.726	C = C	[8, 9, 10, 11]
14	1899.4	42.806	C = C	[8, 9, 10, 11]
15	1973.3	97.387	-	-
16	2055.0	62.660	Isothiocyanate	[8, 9]
17	2144.2	71.735	Azide	[8, 9]
18	2221.5	75.249	Aromatic nitrile	[8, 9]
19	2298.1	90.121	P – H	[8, 9]
20	2373.9	70.531	P – H	[8, 9]
21	2573.4	62.664	Th iol	[8, 9]
22	2916.4	315.583	CH_2	[8, 9, 10]
23	3127.9	307.520	OH	[8, 9]
24	3266.6	57.764	Alkyne	[8, 9]
25	3326.7	91.300	Amide , Amine	[8, 9]
26	3393.4	47.349	Phenol	[8, 9]
27	3567.0	97.917	O – H	[8, 9]
28	3718.0	43.044	-	-
29	3838.1	90.297	-	-

Through the analysis of the five samples it was found that the vibration modes of some materials are appeared in all of samples while some are appeared in some samples and disappear in other samples. That is as follows:

1. X metal - O: appeared in the spectrum of (Ajuad) well, with intensity 189.424.

2. C=S: appeared in the spectra of (Ajuad and omalgoura) wells, with different intensities (284.624, 392.974), respectively.

3. Aromatic ring: appeared in the spectra of all samples (Ajuad, Almazara, Safa, omalgoura, shakreen) wells, with intensities (107.198, 95.939, (4.346, 264.39), 168.6, 84.328), respectively.

4. Si – O – Si: appeared in the spectrum of (Ajuad) well, with intensity 52.7.

5. Si – O – C: appeared in the spectra of the (Ajuad, Almazara, Safa, omalgoura) wells, with intensities (17.031, 805.76, 22.715, 429.6), respectively.

6. Sulfonic acid: appeared in the spectra of (Ajuad, omalgoura, shakreen) wells, with different intensities (55.625, 278.486, (19.514, 26.94), respectively.

7. CH_2, CH_3: appeared in the spectra of (Ajuad, Safa, omalgoura, shakreen) wells, with intensities (130.146, 357.039, 980.4, 105.5), respectively.

8. C=C: appeared in the spectra of (Ajuad, Almazara, omalgoura, shakreen) wells, with different intensities (7.627, (919.309, 549.58, 303.52), (258.246, 10.128), (133.242, 78.726, 42.806)), respectively.

9. Aliphatic azo: appeared in the spectra of (Ajuad and Safa) wells, with different intensities (80.19, 988.648), respectively.

10. Aromatic/hetero ring: appeared in the spectra of (Ajuad, omalgoura, shakreen) wells, with different intensities (316.907, 298.032, 152.54), respectively.

11. Anhydride: appeared in the spectra of (Ajuad, Almazara, omalgoura, shakreen) wells, with different intensities (119.052, 200.584, 235.723, 63.829), respectively.

12. Isothiocyanate: appeared in the spectra of (Ajuad, Safa, shakreen) wells, with different intensities (14.285, 9.362, 62.66), respectively.

13. Thiocyanate: appeared in the spectra of (Ajuad and Almazara) wells, with different intensities (106.136, 94.466), respectively.

14. Diazonium salt: appeared in the spectrum of the recorded from Ajuad well, with intensity 64.756.

15. P – H: appeared in the spectra of (Ajuad, Safa, omalgoura, shakreen) wells, with different intensities (178.422, 0.267, 53.703, (90.121, 70.531)), respectively.

16. Thiol: appeared in the spectra of (Ajuad, Almazara, Safa, shakreen) wells, with different intensities (435.845, 302.806, 50.881, 62.664), respectively.

17. C – CH_3: appeared in the spectra of (Ajuad, Safa, omalgoura) wells, with different intensities (412.409, 83.639, 176.172), respectively.

18. Aromatic C – H: appeared in the spectra of (Ajuad, Safa) wells, with different intensities (191.291, 181.612), respectively.

19. = CH_2: appeared in the spectra of (Ajuad and Almazara) wells, with different intensities ((285.78, 409.05), 418.33), respectively.

20. OH: appeared in the spectra of (Ajuad, Almazara, Safa, omalgoura, shakreen) wells, with different intensities (642.707, 917.323, 543.583, 750.901, 307.520), respectively.

21. Amide, Amine: appeared in the spectra of (Ajuad, Safa, omalgoura, shakreen) wells, with different intensities (620.887, 555.915, 864.619, 91.3), respectively.

22. Phenol: appeared in the spectra of (Ajuad, Almazara, Safa, omalgoura, shakreen) wells, with different intensities (235.57, 213.193, 113.235, (121.918, 32.9), 47.34) respectively.

23. Alkyne: appeared in the spectra of (Almazara, Safa, shakreen) wells, with different intensities (309.899, 60.049, 57.764), respectively.

24. C = N, Lactone, Aldehyde, Alcohol: appeared in the spectrum of (Safa) well, with intensities (2.684, 153.28, 55.579, 48.588), respectively.

25. Azide: appeared in the spectrum of (Safa and shakreen) wells, with different intensities (54.347, 71.735), respectively.

26. N – CH_3: appeared in the spectrum of (Safa and omalgoura) wells, with different intensities (56.932, 39.693), respectively.

27. O – H: appeared in the spectrum of the recorded from (Safa, omalgoura, shakreen) wells, with different intensities (28.316, 181.847, 97.917), respectively.

28. Ester: appeared in the spectra of (omalgoura and shakreen) wells, with different intensities (44.896, 16.037), respectively.

29. Sulfonamide, Aromatic azo, Aromatic nitrile: appeared in the spectrum of (shakreen) well, with intensities (28.230, 166.729, 75.249), 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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