Liquid explosives detection in transparent containers

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Abstract. The principal possibility to recognize liquid explosives and their components in various glass and plastic containers with different transparency in visible spectral range was demonstrated. Acetone was used as a target, as alone and mixed with traditional liquids. The advantage of gated Raman spectroscopy over the CW was proved. It was found that using 532 nm, 6 ns laser pulses any real target with characteristic Raman spectrum with intensity similar to those for acetone may be detected in 100 % of glass and in 80 % of plastic containers. The mixing with different liquid makes detection more difficult and acetone was detected in 55 % of studied cases. The main reasons for detection difficulties are intrinsic Raman and luminescence of plastic containers and liquids relevant to airport passengers. In case of strong luminescence the advantages of red light excitation over green light was demonstrated.

1. Introduction

The constant threat of terror attack on civilian targets emphasizes the need to develop a sophisticated means of detecting explosive materials in different aggregations phases and amounts. Lately terror organizations enhance their efforts of delivering attacks using bombs camouflaged to fine alcohol hoping a security services won't open a several hundred's dollar worth bottle. Thus there is a demand for simple and reliable device for chemical analysis of liquids inside sealed bottles. Detection of liquid explosives inside of different kind of transparent or semitransparent containers requires the development of new analytical techniques. A suitable analytical instrument must be able to detect and identify in almost real-time the explosive liquids materials with a reasonable level of confidence. It is well recognized that laser-based spectroscopy is the proper technique, which may be potentially capable for this purpose in airport scenario. Laser Induced Luminescence and Laser excited Raman scattering may be proposed as suitable for this purpose. In most cases the liquids

luminescence spectra are broad and not specific enough, thus luminescence may not be used alone but must be combined with Raman spectroscopy. Several Raman based devices were proposed recently for liquid detection inside containers, but all of them are based on continuous wave (CW) Raman technique [1,2]. It is well known that luminescence of bottles and liquids may interfere with CW Raman measurements. Gated Raman spectroscopy technique using a visible laser for excitation seems to be very promising for our goal showing several advantages over CW Raman [3].

The aim of this paper was to check the ability of our laboratory gated Raman system to recognize acetone and its mixtures with relevant liquids, such as wines, oils and different soft drinks, in more than 60 transparent and semitransparent glass and plastic vessels. The intensity of acetone Raman spectrum was compared with some liquid explosives components, such as nitromethane, hydrogen peroxide and different acids to check our ability to develop a real detector. Several excitation wavelengths in visible diapason have been compared.

2. Experimental technique

The detailed description of the experimental system was presented elsewhere [3]. The sample holder was modified to contain different kinds of bottles. Two excitation sources were used: (i) second harmonic of Continuum Micro-Light Nd-YAG (532 nm, 6 ns, 40 mJ) and (ii) tunable Opotek's Opolette 355 Optical Parametric Oscillator (OPO) in spectral range from 0.410 μm up to 2.5 μm with pulse duration about 6 ns and laser pulse energy about 1 mJ. The experiment was performed with two different CCD exposure times: gate widths – 10 ns for gated Raman measurements and 9 ms for a quasi-continuous Raman. In the gated Raman experiment a gate width is of the order of magnitude of laser pulse, so the much longer luminescence processes interfere less than in quasi-continuous experiment, where the luminescence has much greater influence. It's important to emphasize that both measurements were performed in exactly the same physical conditions. Both empty and filled bottles were measured. All Nd-YAG measurements were performed averaging over a 100 laser pulses. In the case of OPO excitation averaging was over 1000 laser pulses due to weakness of laser pulse. Raman signals intensity is measured from the base of the

line on broadband background. Signal to Noise (S/N) was evaluated as a ratio of the normalized intensity to the electronic noise of the detection system. The transmittance spectra have been measured using the container pieces from different bottles by Jasco spectrophotometer (model V-530) in 400-1000 nm spectral range. The numerical transmittance data are presented for 535 and 590 nm points, which represent the limits of the spectral range where Raman spectrum has been measured.

3. Experimental results

3. 1. Raman spectra of acetone in glass bottles

Mainly acetone was selected as a target compound for this study and sometimes ethanol and acetone/ethanol mixtures were used. Table 1 represents the types of studied glass containers and Figures 1, 2 their typical transmittance spectra and Raman spectra of acetone inside those containers.

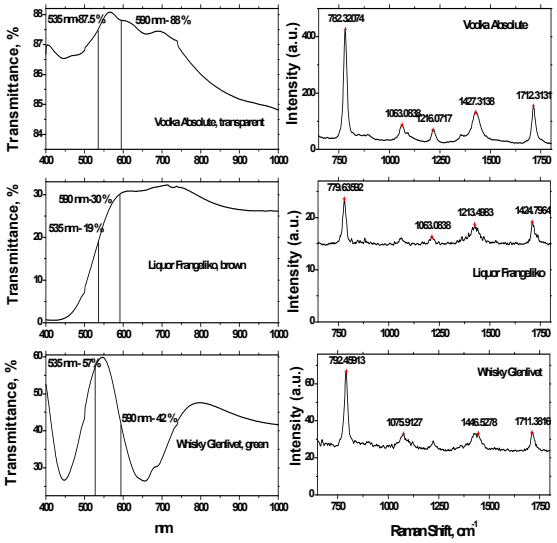

Figure 1. Transmittance spectra of transparent, brown and green bottles and Raman spectra of acetone inside those containers.

Table 1. The studied glass bottles and the main Raman line of acetone intensity

N	Name	Color	Transmittance, %	Normalized Intensity au	S/N
1	Vodka Absolute	Transparent	87.5-88	400	100
2	Vodka Smirnoff	Transparent		580	150
3	Shablis Red Wine	Greenish		260	75
4	Sardasol, Red Wine	Green		180	50
5	Frangeliko Liquor	Brown	19-30	10	10
6	Bacardi Breezer Lemon	Transparent		1600	500
7	Bacardi Breezer Melon	Transparent		1760	500
8	Beer Grolsch	Green		420	100
9	Malt Nesher	Brown	10-28	30	15
10	Gerber Juice Pear	Transparent		125	100
11	Liquor Coffee	Transparent		150	50
12	Kikkoman	Transparent		30	75
13	Olive Oil	Transparent		20	50
12	Perfume NafNaf	Red	17.2-17.5	30	10
13	Arak	Transparent		100	25
14	Perfume Love Line	Red	1.5-11.5	55	15
15	Cream Revlon Absolutes	Dull	9.5-10	110	50
16	Malt Glenlivet	Green	57-42	40	15
17	Perfume Toxic	Red	5-16	20	10
18	Perfume Dee Deep	Red	5-15.5	40	15

In all glass containers acetone was definitely detected by its characteristic Raman lines. Both the strongest line peaking at 782 cm^{-1} and the weaker lines peaking at 1063, 1216, 1427 and 1712 cm^{-1} may be seen, which makes the identification ability very high and the false rate actually zero. The intensity of the main Raman peak is changing from approximately 1800 to 25 arbitrary units depending on transmittance of the corresponding glass in the spectral range of 535-590 nm, which is relevant for Raman lines. The lowest intensities were detected for brown and red glasses. No one of the studied glass materials revealed strong luminescence in 535-590 nm spectral range using gated Raman technique, while it is the main obstacle for traditional CW Raman. Only one red glass exhibits detectable luminescence. Studied glass bottles mostly do not exhibit strong intrinsic Raman

lines. The only exception with detectable Raman line near 1094 cm^{-1} is red perfume bottle (Fig. 2), but it is very weak and will not prevent Raman identification of the future target compounds. Because those containers do not reveal their own luminescence or Raman signals, even one Raman line of suspicious material in any part of the Raman spectrum (400-3000 cm^{-1}) will be enough. Comparing the gated and not gated spectra it was found that for glass the short-gated spectra have major advantage over quasi-continuous ones (Fig. 3). There is a much weaker luminescence that can mask a Raman signal in the short-gated spectra. It appears that while gated Raman demonstrates no differences between various bottles presenting a strong and clear quartz lines, the quasi-continuous spectra present clear variations connected with intrinsic luminescence. Acetone and ethanol have been measured inside glass bottles by gated and not gated modes. In such scenario, we have to move the focus inside the bottle. It makes the signal coming from the walls weaker while the main signal comes from the liquids. Thus, the glass material which bottles are made of is less important as long as it is transparent for the visible light. Nevertheless, comparison between the gated Raman spectra and actually not-gated demonstrates that gating enables to remove totally the interference from bottle material luminescence and Raman signatures are much clearer, allowing to better detect and recognize the substance inside the bottle (Fig. 4).

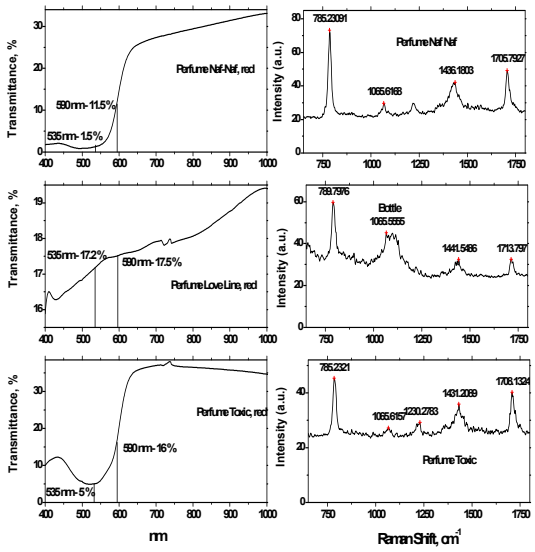

Figure 2. Transmittance spectra of red bottles and Raman spectra of acetone inside those containers.

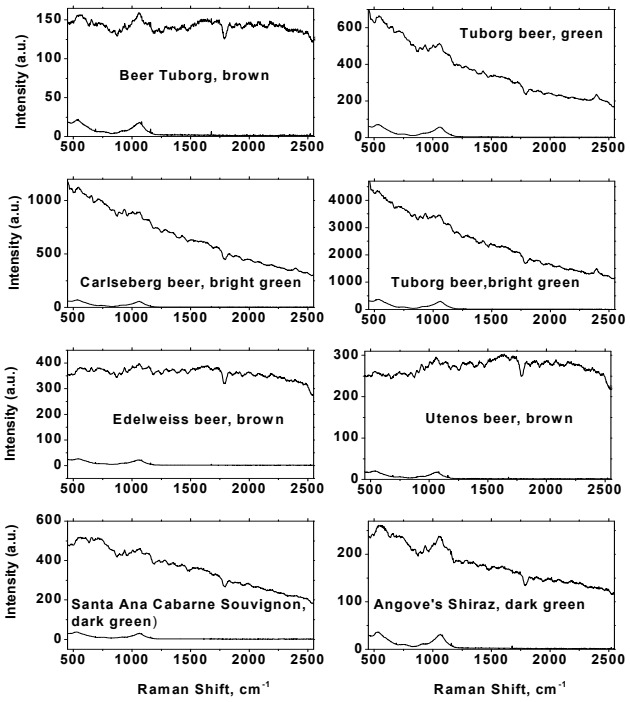

Figure 3. Raman spectra of different glass bottles with gating of 10 ns (low line) and without gating (upper line).

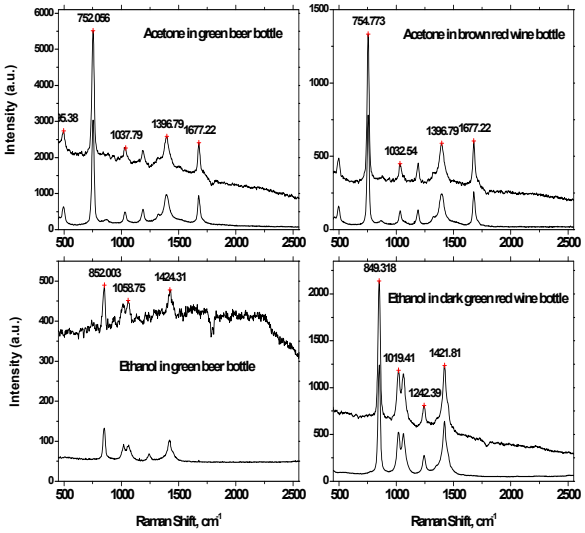

Figure 4. Raman spectra of acetone and ethanol in different glass bottles with gating of 10 ns (low line) and without gating (upper line).

3. 2. Raman spectra of acetone in different plastic bottles

Actually all plastic containers exhibit very strong luminescence under excitation by 532 nm both in not gated and gated modes. Nevertheless the gated technique enables to substantially reduce the luminescence interference (Fig. 5). Table 2 represents the types of studied plastic containers and Figures 6, 7 their typical transmittance spectra and Raman spectra of acetone inside those containers. Opposite to the glass containers, acetone was definitely detected by its characteristic Raman lines only in 26 plastic bottles from 35 while in two bottles only the strongest acetone Raman line may be identified because of influence of intrinsic plastic Raman. Thus acetone may be detected in 28 from 35 plastic containers (80 %). The intensity of the main Raman peak is changing from ~ 300 to 0 arbitrary units. The lower maximal intensity compared to glass containers is connected to substantially lower (~ 100 times) excitation energy which may be used for Raman excitation. The reason is plastic burning under excitation density more than 1 MW/cm^2. It appears that the main reason when the identification is not possible is not the low transparency of plastic containers, but their intrinsic Raman and luminescence. In our experiments it appears that focusing laser light inside the plastic bottle partly prevent the bottle burning but not improve Raman signal quality. The identification of acetone was not possible in seven plastic bottles. In two of them the intrinsic Raman is so strong that it covers the target compound Raman. In other five bottles the strong luminescence even using gated Raman technique prevents detection.

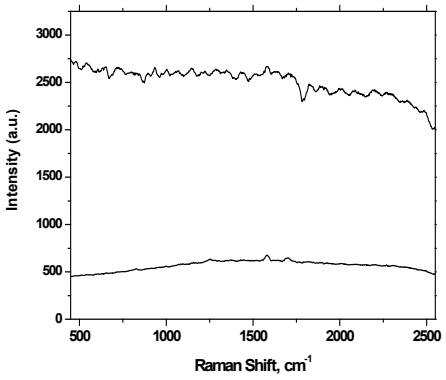

Figure 5. Typical Raman spectra of plastic bottle with gating of 10 ns (low line) and without gating (upper line).

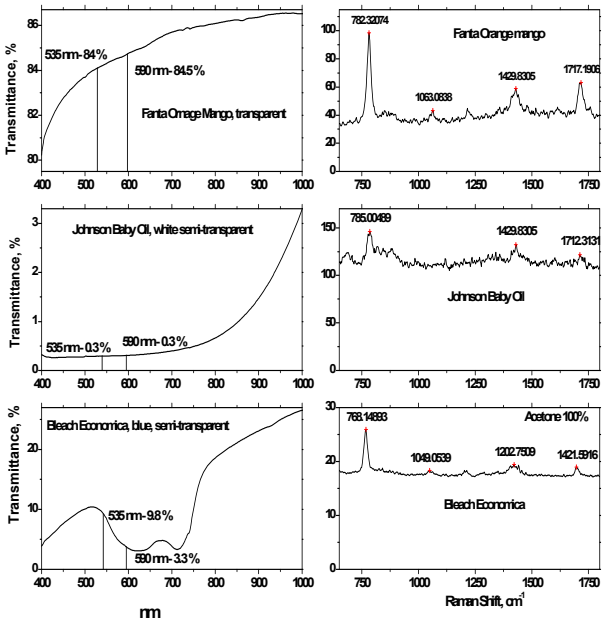

Figure 6. Transmittance spectra of transparent, white and blue semi-transparent plastic bottles and Raman spectra of acetone inside those containers.

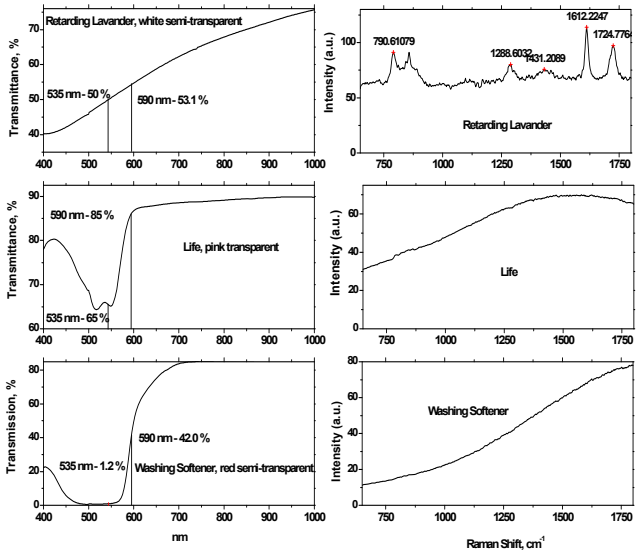

Figure 7. Transmittance spectra of white, pink and blue semi-transparent plastic bottles without Raman spectra of acetone inside those containers.

Table 2. The studied plastic bottles and the main Raman line of acetone intensity

N	Name	Color	Transmittance, %	Normalized Intensity, au	S/N
1	Fanta Orange Mango	Transparent	84.0-84.5	70	35
2	Primor Fruit Juice	Transparent		140	75
3	Tapuzina Diet	Transparent		190	100
4	Prigat Apple Honey	Transparent		25	20
5	Baby Oil	Transparent		135	70
6	Sod Max	Transparent		100	60
7	Johnson Baby Oil	White	0.3 – 0.3	10	3
8	Glass Cleaner	Transparent		170	50
9	Nestea Mango Apple	Transparent		80	10
10	Tapuzina Fresh Apple	Transparent		90	12
11	Prigat Citrus Honey	Transparent	73.7 – 74.1	30	15
12	Pepper Mouth Wash	Transparent		30	30
13	Cool Mint Mouth Wash	Transparent		25	25
14	Coca Cola Zero	Transparent		30	20
15	Fairy Original	Transparent		60	50
16	Pashtan Oil	Transparent		15	25
17	Canola Oil	Transparent		20	20
18	Bleach Economica	Bluish	9.8-3.3	7	5
19	Retarding Lavender	White	50-53.1	0	0
20	Souse Soya	Transparent	88-88.2	0	0
21	Life	Pink	65-85	0	0
22	Life	Blue	82-73	100	100
23	Life	Purple		120	80
24	Life	Transparent		150	125
25	Body Wash	Transparent		120	100
26	Bath Gel	Transparent	86.5-87	27	20
27	Body Scrub	Transparent		32	25
28	Thai Sweat Chili Sauce	Purple		40	35
29	Pachuki Lavander	Purple		10	5
30	Shock	White		20	15
31	Vaseline	White	0.55-0.65	0	0
32	Washing Softener	Purple	10-12	0	0
33	Body Lotion	Pink	42.5-71	0	0
34	Washing Softener	Red	1.2-42	0	0
35	Empty Keter	Transparent		70	75

3. 3. Raman spectra of acetone in glass bottle mixed with different liquids

Table 3 represents the types of studied mixtures and Figure 8 their typical Raman spectra inside transparent glass bottle. The identification probability becomes lower compared to identification in empty bottles. Acetone was definitely detected in mixtures with 18 liquids from 34 while in mixtures with 14 liquids only the strongest acetone Raman line may be identified and the detection is potentially possible, but very difficult. In mixtures with two liquids the detection is impossible. The reasons for the difficult detection are the influence of intrinsic liquids Raman and luminescence.

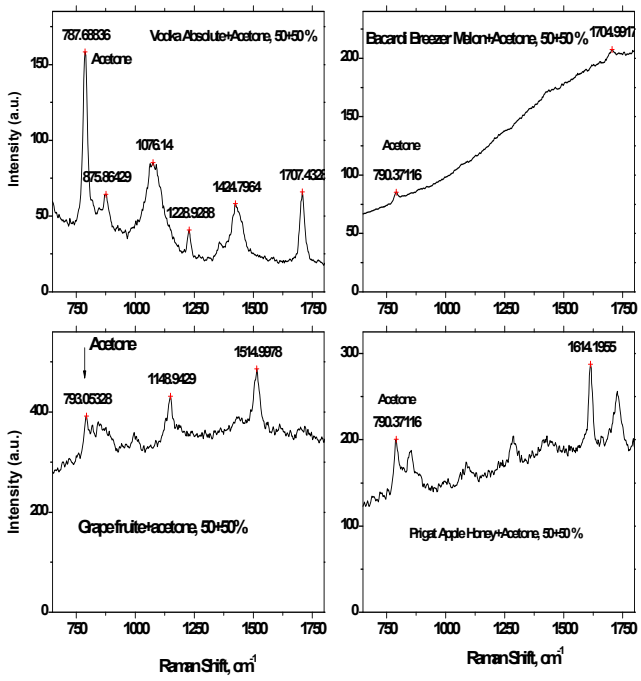

Figure 8. Typical Raman signal of liquid-acetone mixtures measured in transparent glass bottle.

All studied liquids are characterized by very strong luminescence with relatively weak ethanol lines for alcohol drinks. This strong luminescence present both in gated and in quasi-continuous modes, but it is several times lower for the first technique (Fig. 9). Thus common liquids that can be transported in passenger's luggage present a strong luminescence when excited by 532 nm

wavelengths. This luminescence can mask the signal coming from explosive or other potentially dangerous materials. One known way to avoid luminescence excitation is to use red or NIR excitations. We checked several liquids with intensive luminescence using different excitation wavelengths and arrived to conclusion that such approach may be really helpful. For example, Figure 10 represents cognac luminescence spectra under different visible excitations. It may be seen that cognac exhibits slightly different luminescence with different excitations. The band's maximum is at 500, 540 and 580 nm for 410, 480 and 532 nm excitations, respectively. The excitation spectra present a clear tendency of growing luminescence intensity towards the blue region. This tendency takes place both for measurements at the center of luminescence band and for the off-center ones. Starting from excitation by 590 nm the cognac luminescence becomes very weak. Similar behavior was found for other alcohol liquids, such as whisky. In red wine, however, the luminescence behavior is different and the band's center is constant peaking at 650 nm (Fig. 11). But once again, starting from excitation by 590 nm the red wine luminescence becomes very weak.

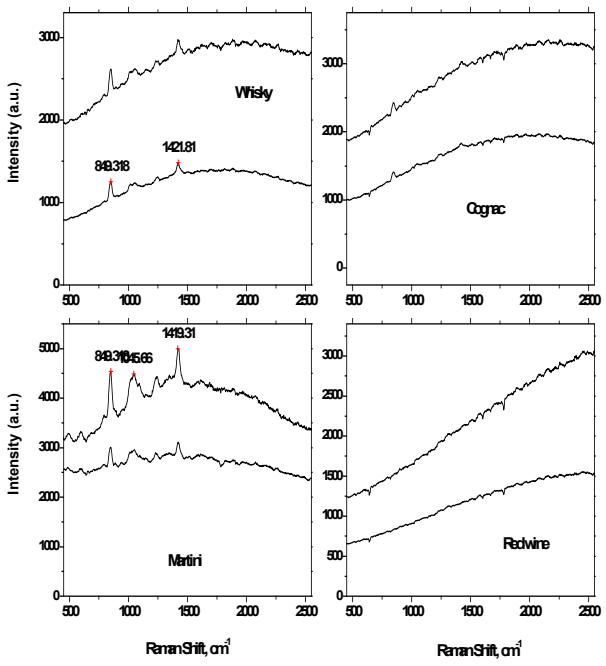

Figure 9. Raman spectra of several non-explosive liquids in transparent glass bottle with gating of 10 ns (low line) and without gating (upper line).

Table 3. The studied mixtures of acetone and liquids

N	Name	Normalized Intensity au	S/N
1	Vodka Absolute	110	100
2	Vodka Smirnoff	275	150
3	Shablis Red Wine	125	75
4	Sardasol, Red Wine	6	3
5	Frangeliko Liquor	10	10
6	Bacardi Breezer Lemon	80	50
7	Bacardi Breezer Melon	10	10
8	Beer Grolsch	30	15
9	Malt Nesher	5	5
10	Fanta Orange Mango	45	25
11	Grape Fruit Juice	50	25
12	Tapuzina Diet	65	50
13	Prigat Apple Honey	50	25
14	Gerber Juice Pear	40	15
15	Baby Oil	20	10
16	Sod Max	15	10
17	Johnson Baby Oil	25	15
18	Glass&Window Cleaner	50	25
19	Nestea Mango Pine Apple	35	20
20	Tapuzina Fresh Apple	60	25
21	Whisky Glenlivet	70	45
22	Liquor Coffee	150	50
23	Prigat Citrus Honey	10	10
24	Pepper Mint Mouth Wash	10	10
25	Cool Mint Mouth Wash	10	10
26	Coca Cola Zero	0	0
27	Fairy Original	50	25
28	Kikkoman	0	0
29	Olive Oil	15	10
30	Pashtan Oil	12	10
31	Canola Oil	13	10
32	Bleach Economica	10	10
33	Arak	65	25
34	Perfume Love Line Rouge	5	5

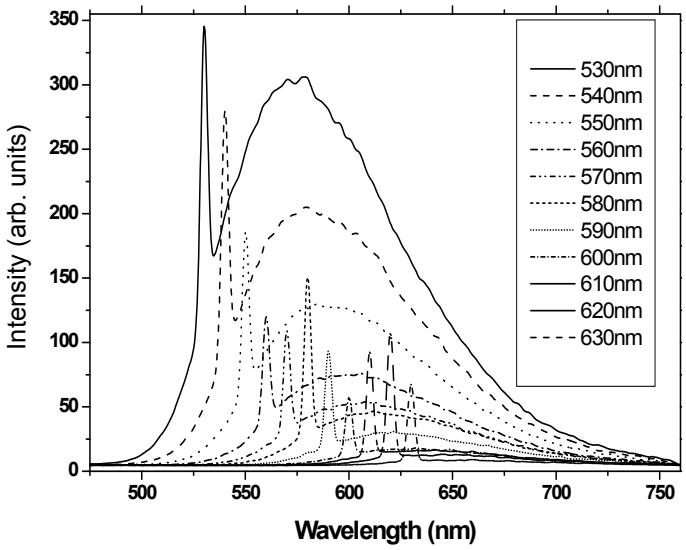

Figure 10. Cognac luminescence with different excitations (sharp picks are laser excitation lines).

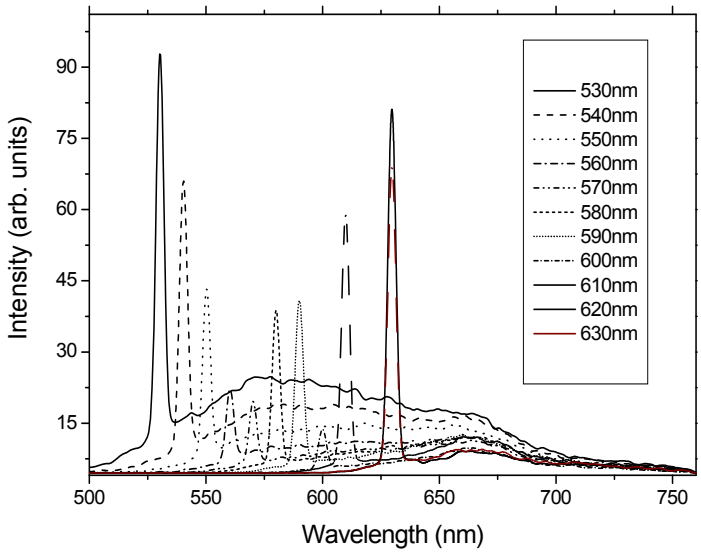

Figure 11. Red wine luminescence with different excitations. (Sharp picks are laser excitation lines).

It may be concluded that application of red and not green Raman excitation appears preferable to overcome the luminescence interference. Thus we start to check the red Raman spectra of several

from studied objects. Figure 12 demonstrates such spectra for acetone and ethanol. In contrast with excitation by 532 nm, the difference between short gated and long gated spectra is substantially less. Relatively strong luminescence exists under red excitation also, but its influence is less prominent. For example, under excitation by 532 nm almost no intrinsic ethylene Raman signal was visible on strong luminescence background in alcohol drinks, while it may be seen even in red wine spectrum, while in cognac, whiskey and white wine they are strong and clear (Figure 13).

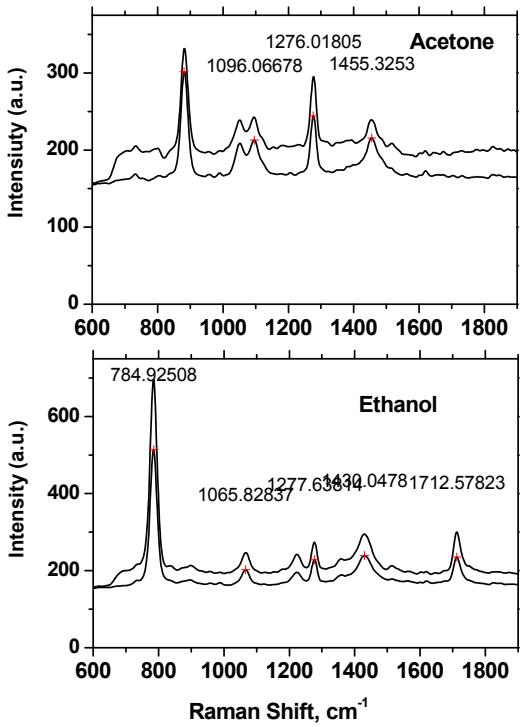

Figure 12. Raman spectra of acetone and ethanol under excitation by 650 nm in transparent glass bottle with gating of 10 ns (low line) and without gating (upper line).

3.4. Raman spectra of TNT and RDX dissolved in acetone and ethanol

The Raman spectra of TNT and RDX diluted in acetone and ethanol have been studied. Comparing those four different possibilities for explosive solution demonstrates that the most

recognizable features relate to TNT solution in acetone, evidently due to good dissolving properties of acetone and strong TNT Raman signal. Example of such spectra are presented in Figure 14. Subtracting a pure acetone spectrum from TNT-acetone mixtures and plotting the highest TNT peak (ν = 1326 cm^{-1}) height against the TNT concentration, the good linear correlation was received between TNT concentration and its Raman signal (Fig. 15). It may be concluded that it is possible to detect TNT mixtures in acetone down to a concentration of 10 mg/cm^3.

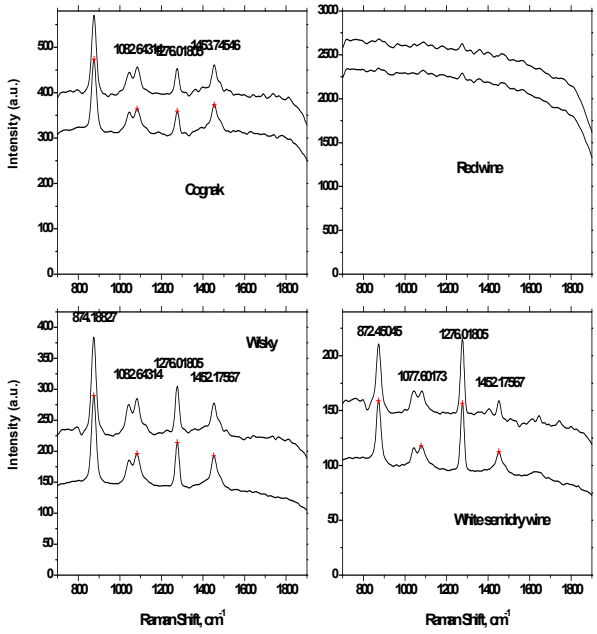

Figure 13. Raman spectra of several non-explosive liquids under excitation by 650 nm in transparent glass bottle with gating of 10 ns (low line) and without gating (upper line).

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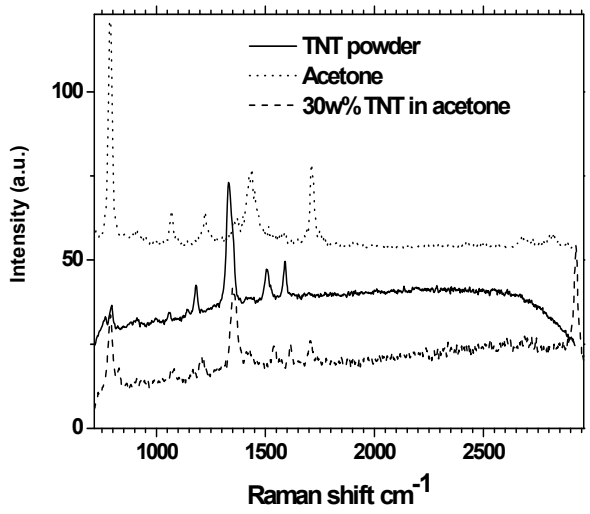

Figure 14. Raman spectra of TNT, acetone and 30 % TNT solution in acetone

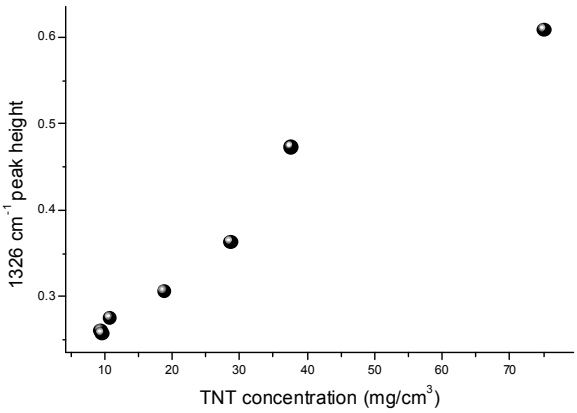

Figure 15. Correlation between Raman signal of TNT and its concentration in acetone

Other mixtures show worse results. The ratio between the RDX and acetone peaks is relatively small even for high concentrations of RDX. The same picture is for TNT solution of ethanol – only in saturated solution the TNT spectral fingerprint can be clearly seen. The worst case is RDX solution in ethanol. The poor diluting power of ethanol combines with the fact that the highest RDX peak overlaps with highest ethanol peak and consequently even in saturated solution no RDX features can be clearly seen.

3.5. Raman spectra of liquid and solid explosive components

Figures 16 and 17 demonstrate Raman spectra of some potentially dangerous liquids components measured at the same experimental conditions. It may be seen that fortunately all have specific Raman signatures with intensity similar to those for acetone, which makes Raman spectroscopy a potential tool for their identification inside transparent containers.

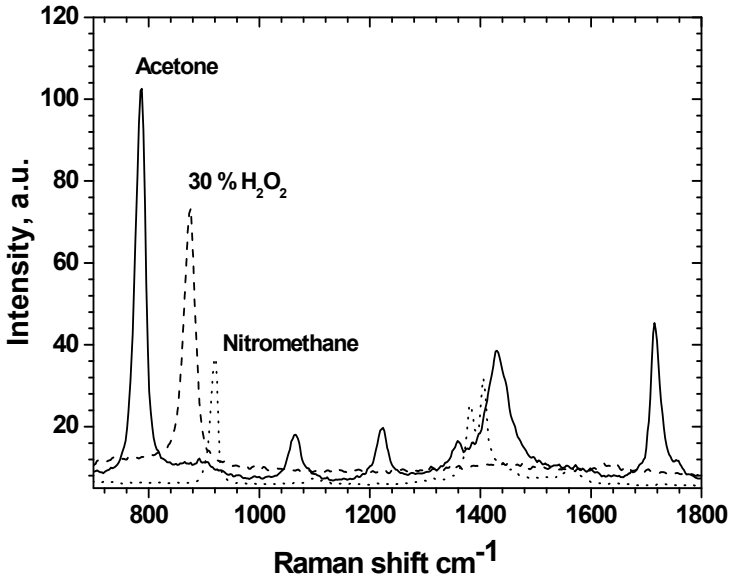

Figure 16. Raman spectra of acetone, 30% solution of hydrogen peroxide and nitromethane

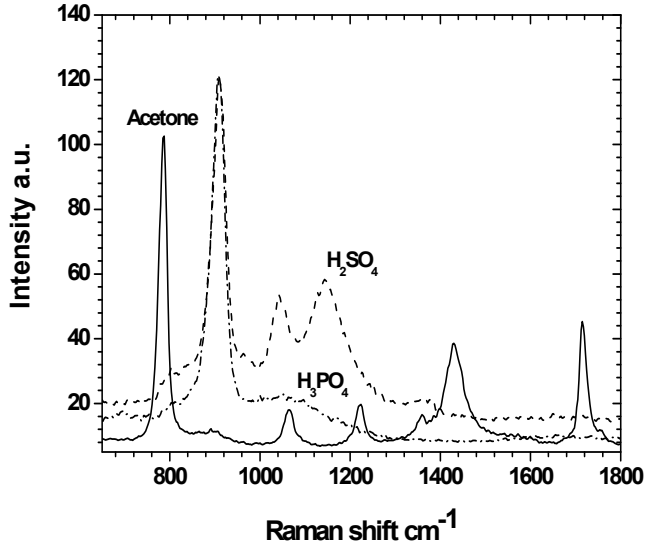

Figure 17. Raman spectra of acetone, H_2SO_4 and H_3PO_4 acides

4. Conclusions

This study was devoted to Raman detection of pure acetone in different glass and plastic containers, and of acetone mixed with different liquids in transparent containers. Laboratory device used for this task includes excitation laser (second harmonic, 532 nm, 6 ns) and gated ICCD iStar detector. Seventeen glass containers with different transparencies and colors have been tested. Acetone was detected in 100 % of them. Thirty five plastic containers with different transparencies and colors have been tested. Acetone was be detected in 80 % of them. Thirty-four different liquid mixtures with acetone in transparent containers have been tested. Acetone detected in 55 % of them.

The main obstacle for acetone detection is strong intrinsic luminescence of certain plastics and liquids under excitation by 532 nm. Gated Raman technique with red excitation with optical parametric oscillator (OPO) pulsed laser as excitation source is evidently the better approach. Besides better luminescence removing, plastic materials are burning under green excitation density more than 1 MW/cm^2. Lower excitation intensities lead to relatively weak Raman signals. Once again, using less energetic red excitation may help to overcome this problem.

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