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A rapid method for screening and determination test of methanol content in ethanol-based products using portable Raman spectroscopy

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ABSTRACT

Raman spectroscopy is nondestructive sample preparation and suitable for use in quality control-related field inspections, particularly on ethanol-based products. The influence of laser power density (PD) and exposure time (ET) on the Raman spectra similarity, specificity, selectivity, and accurate measurements for screening and determination of methanol content were carried out in this study.

Raman spectra of samples were measured using a Raman handheld instrument. Measuring scales of PD and ET were varied from 50 to 300 milliWatt (mW) and 1000–5000 ms (ms), respectively. The similarity of Raman-spectra of those samples was statistically analysed with the help of hierarchical cluster analysis (HCA) and cross-correlation function (C_{correl}). The subtracted Raman spectra and pure ethanol spectra were implemented to identify methanol content in samples of ethanol-based products specifically.

The Raman spectra measured at PD of 200–300 mW and clustered in one group by ward linkage method showed a similarity level of 99.98%. The variation of ET between 1000 and 5000 ms on fix PD of 300 mW showed high precision (RSD < 2%) with more than 99% similarity of Raman spectra. Rinsing of PD was found to increase the signal: noise ratio, while prolonged exposure time reduced the signal: noise ratio. The precision and accuracy measurements were obtained by setting the PD and ET values of 300 mW and 4000 ms, respectively. The subtracted Raman spectra with the spectra of absolute ethanol introduced a simultaneous screening of methanol containing alcohols and determination of both substances.

1. Introduction

Raman handheld spectroscopy is a portable analytical instrument and recently has become more popular due to its simplicity in terms of nondestructive and no requirement on specific sample preparations). This method also provides characteristic spectra of substances contained in tested materials, and therefore it has been implemented in the qualitative and quantitative assessment of a variety of illicit substances of forensic interest, impurities in pharmaceutical preparations, and biochemical analysis and diagnosis [1,2]. The quality of analytical processes of such impurities is characterised by specificity, selectivity, sensitivity, and accuracy [3]. Its sensitivity and accuracy depend on the measured Raman scattered signals. These signals are products of the controlled instrumental factors, geometrical measurement factors, numbers of molecules in the sampled region, and the measured Raman scattering signals on the detector [4]. The controlled instrumental

Abbreviations: % v/v, percent volume/volume; $C_{pEt\text{-}S}$, the cross-correlation function coefficient of comparison between Raman spectrum of pure ethanol and sample; $C_{pMe\text{-}S}$, the cross-correlation function coefficient of comparison between Raman spectrum of pure methanol and sample; C_{correl}, cross-correlation function coefficient; CCα, decision limit; CCβ, capability of detection; $C_{sM\text{-}sS}$, the cross-correlation function coefficient of comparison between the subtracted Raman spectrum of methanol with spectrum of ethanol and the subtracted Raman spectrum of sample with ethanol spectrum in range of 950–1150 cm^{-1} detection limit; ET, exposure time; HCA, hierarchical cluster analysis; LQ, limit of quantification; ms, milliseconds; mW, milliWatt; PD, laser power density; RSD, Relative standard deviation; S/N, signal to noise ratio; S_y, the residual standard deviation; V_{xo}-value, the relative process standard deviation

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factors include the PD and the ET.

In Indonesia, illicit alcohol "*oplosan*" is made by mixing fruit soft drinks and water, and its desired alcohol concentration is adjusted by adding technical ethanol. This type of alcoholic beverage has been reported to cause health problems in Estonia, Norway, Turkey, Brazil, China, India, and Indonesia, as the origin of such beverage is unknown [5]. Methanol often contaminated the technical ethanol used in the process of making *oplosan*, which is dangerous for human health. Therefore, a rapid method to detect and determine the presence of methanol in ethanol-based products, including *oplosan* is urgently needed. The Raman spectrophotometer appears to be appropriate for such purposes as it has been widely implemented to determine methanol content in alcoholic beverages [5]. The labelling errors between food grade alcohol and technical methanol by wholesalers introduced fatal production of *oplosan*. Raman handheld spectrophotometer offers *in-situ* quality control of ethanol, methanol, or illegal alcoholic beverages for forensic purposes. Implementation of this equipment in forensic toxicology analysis should be able to screen and determine the presence of methanol in such products. In the screening, a Raman spectrophotometer should be able to specifically differentiate ethanol and methanol and shows sensitive determination on both substances. In this study, optimisation of the Raman handheld analyser used for identification and determination of methanol and ethanol influenced by variations of PD and ET in the identification and quantification of methanol and ethanol was investigated. The main aim of this study was to develop a simple and rapid non-destructive method for quantification and identification of ethanol and methanol in various alcoholic products by using Raman portable instrument.

2. Materials and methods

2.1. Chemicals and materials

Analytical grade alcohol and methanol (products of Merck-Germany) were used in this study. Ethanol-based antiseptics and disinfectants were bought from local pharmacies or chemical wholesales, while rice-wine (*arak*) was obtained from a local store.

The equipment used in this study included FirstGuard™–Handheld Raman Analyzer-USA, and glassware (IWAKI-Pyrex-Indonesian).

2.2. Sample preparation

Absolute ethanol or methanol was placed in vial cuvettes, and their Raman spectra were measured by varying PD and ET values of the instrument. The laser wavelength was 1064 nm. On the variation PD series experiments, the PD was varied between 50 and 300 mW and the ET was fixed at 1000 ms (ms). On the other series of experiments, the PD value was fixed at 300 mW, and the ET values were varied between 1000 and 5000 ms. Triplicate measurements were conducted for each Raman spectrum. The similarity levels among spectra were determined by using hierarchical cluster analysis (HCA) with ward linkage-correlation coefficient distance and cross-correlation function (C_{correl}). The signal to noise ratio (S/N) and detection limit (DL) of the Raman-spectra measurement was then calculated. The noise was collected by measuring a blank solution (0% v/v).

The concentrations of both ethanol and methanol were varied as follows: 99.9%, 96%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, 8%, 6%, and 0.5% (v/v). Triplicate measurements on each concentration level of Raman spectrum on each level of ET (1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500 and 5000 ms) were conducted in the experiment. The similarity of Raman spectra of each concentration level was compared to the Raman spectra of absolute ethanol or methanol on the same series of ET.

Methanol content in ethanol solutions was prepared in four different mixtures. The Raman spectra of mixture solutions were measured at PD and ET values of 300 mW 4000 ms, respectively. The series mixtures used were (A) a series methanol concentrations of 80, 60, 40, 20% (v/v) in absolute ethanol; (B) a series methanol concentrations of 0.5, 1.0, 5.0, and 10% (v/v) in 10% ethanol solution; (C) a series methanol concentrations of 0.5, 1.0, 5.0, and 10% (v/v) in 20% ethanol solution; and (D) a series methanol concentrations of 0.5, 1.0, 5.0, and 10% (v/v) in 30% ethanol solution. The Raman spectra of samples were also measured at various values of PD and ET.

2.3. Data processing

The file of Raman-spectra was compiled and converted into a file of Microsoft excel data with the help of SpectraGryph 1.0, developed by Dr Friedrich Menges-Germany [6]. The Raman-spectra similarity of the absolute methanol and ethanol in various PD values was calculated with the help of HCA-ward linkage method and then analysed with the help of statistical software Minitab 17 ® for windows Cross-correlation function was used to calculate the similarities between the two spectra.

2.4. Validation

Validation of the developed method was based on the screening and determination test criteria under the guidance of UNODC (2009) [7]. The validation parameters included specificity/selectivity, the limit of detection (decision limit "CCα" and capability of detection "CCβ" and quantification limit "QL") [8], precision, linearity, accuracy, recovery, stability. The Limit detection parameters were calculated from linear regression and signal to noise ratio (S/N) methods.

3. Results and discussion

3.1. The PD and ET on Raman screening test

The Raman spectra of the absolute ethanol (Et) and the absolute methanol (Me) in a variation of PD and ET is presented in Fig. 1. The Raman shift peaks of pure ethanol were observed at 427, 880, 1053, 1093, 1274 and 1452 cm^{-1}. The pure methanol present peaks at 1029 and 1465 cm^{-1}. The band arises at 840–1180 cm^{-1} due to the C-O and C–C-O stretching modes and 1200–1750 cm^{-1} covers the CH_2, CH_3, C-OH and HOH binding modes [9]. The bands of the C-O and C-C-O stretching mode are the characteristic Raman frequencies for the ethanol and methanol. This range of Raman shift band could be used for the screening methanol contain in an ethanol-based product.

The HCA results of Raman spectra of pure ethanol and pure methanol under variation of PD are presented at the Fig. 2(a) and (d). The PD values of 200–300 mW showed a similarity of more than 99%. When the PD value was set at 50 mW, the similarity of pure ethanol and methanol with those of standard Raman spectra decreased to 90.94% and 84.0%, respectively (Fig. 1 a and d). The low PD value increased the noise, and this was due to the reduction of the S/N ratio [4]. This resulted in a decline in the similarity between Raman spectra. Dilution of both pure ethanol and methanol with water lead to great spectra deviation when compared to their absolute ones (Fig. 1: b, c, e, and d). The PD value of 300 mW gave the highest similarity value on each concentration solutions. When the system was set at fix PD value of 300 mW and at a various exposure time of between 1000 and 5000 ms, the variation of similarity on each level concentration of both ethanol and methanol became no significant (Fig. 1 c and f). High PD and ET values increased the S/N ratio and gave high inter-spectra similarity values. This provided better conditions for the screening test in combining Raman spectroscopy and chemometric analysis.

Bands appear at 840–1180 cm^{-1} are the characteristic Raman frequencies for both pure ethanol and methanol [9]. All Raman spectra subtracted with the spectrum of absolute ethanol are presented in Fig. 3b. The subtracted Raman spectra of methanol solution and solution of methanol in ethanol provided peaks with λ_{max} at 1029 cm^{-1}, while no peak was observed in the subtracted Raman spectra of ethanol

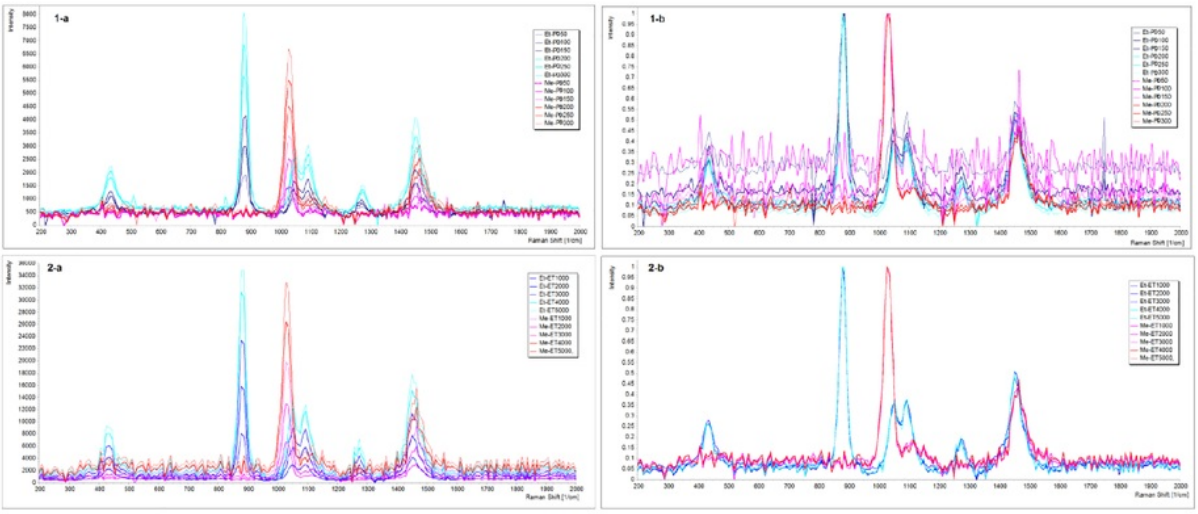

Fig. 1. Raman spectra of the absolute ethanol (Et) and the absolute methanol (Me) in variation of PD (1-a: non-normalized peak; 1-b: normalized peak) and ET (2-a:non-normalized peak; 2-b:normalized peak).

solution [5]. The differences of spectra between pure ethanol and solution of methanol in ethanol or between absolute ethanol and methanol were no peaks observed in the range of 950–1150 cm^{-1}. Comparison of all subtracted spectra to those of the Raman spectrum of pure methanol by cross-correlation function governed various similarity values (Fig. 3c and d). The subtracted Raman spectra of ethanol solution provided C_{correl}-values of less than 47.8%. On the other hand, the C_{correl}-values of the subtracted Raman spectra of methanol solution and solution of methanol in ethanol were found to start from 35% and increase to 100% along with a rising concentration of the methanol. When the subtracted Raman spectra of diluted methanol and absolute ethanol or absolute methanol were compared, they presented C_{correl}-values of 97–100%. As shown in this Figure that the ethanol solution produced C_{correl}-values of less than 35%, while methanol containing

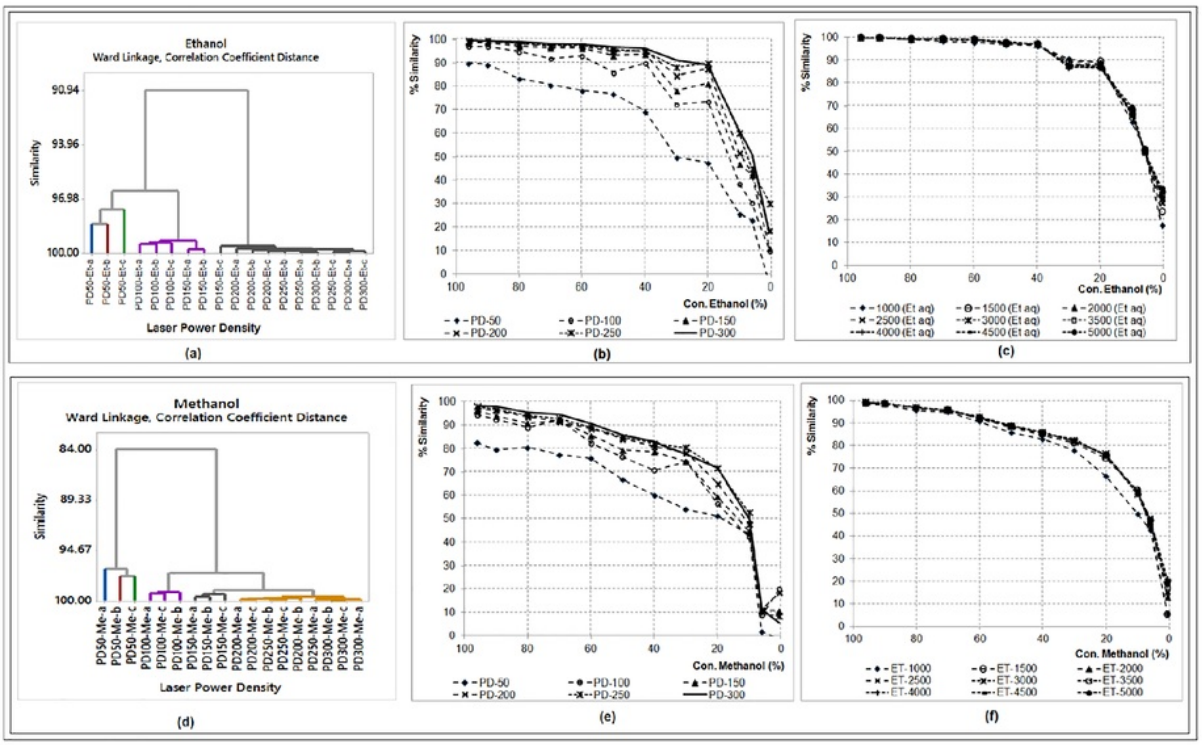

Fig. 2. The Similarity values of Raman spectra influenced by PD and ET Variations. (a and d): the influence of PD on Dendrogram of clustering Raman spectra of absolute ethanol and methanol; (b and e): the influence of PD on the similarity levels of ethanol and methanol solution; (c & f): the influence of ET on the similarity levels of ethanol and methanol solution.

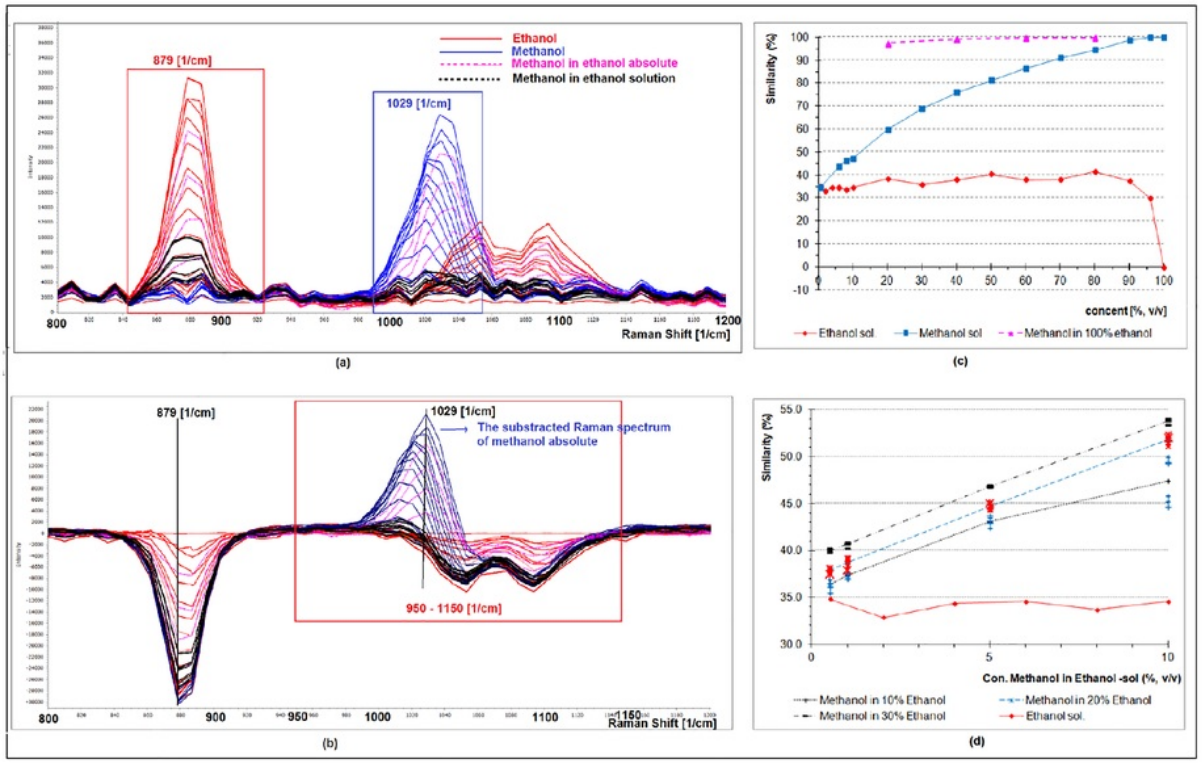

Fig. 3. The Raman spectra of ethanol solution and diluted methanol in ethanol (a–b) and their similarity level (c–d). (a) The Raman spectra of ethanol solution (red line), methanol solution (blue line) and the ethanol contained methanol series solutions (pink and black dotted lines); (b) The subtracted Raman spectra with absolute ethanol spectrum; (c) The similarity level of the subtracted Raman spectra in compare to the subtracted Raman spectrum of absolute methanol; (d) The similarity levels of the subtracted Raman spectra of methanol in ethanol solution.

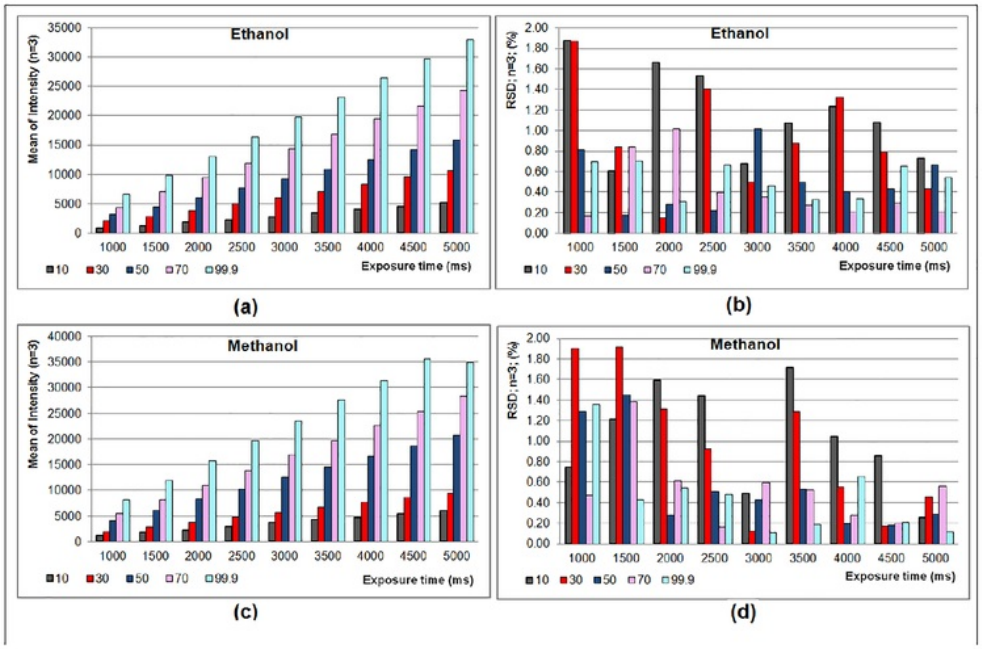

Fig. 4. The mean and RSD measurements of Raman in various exposure times.

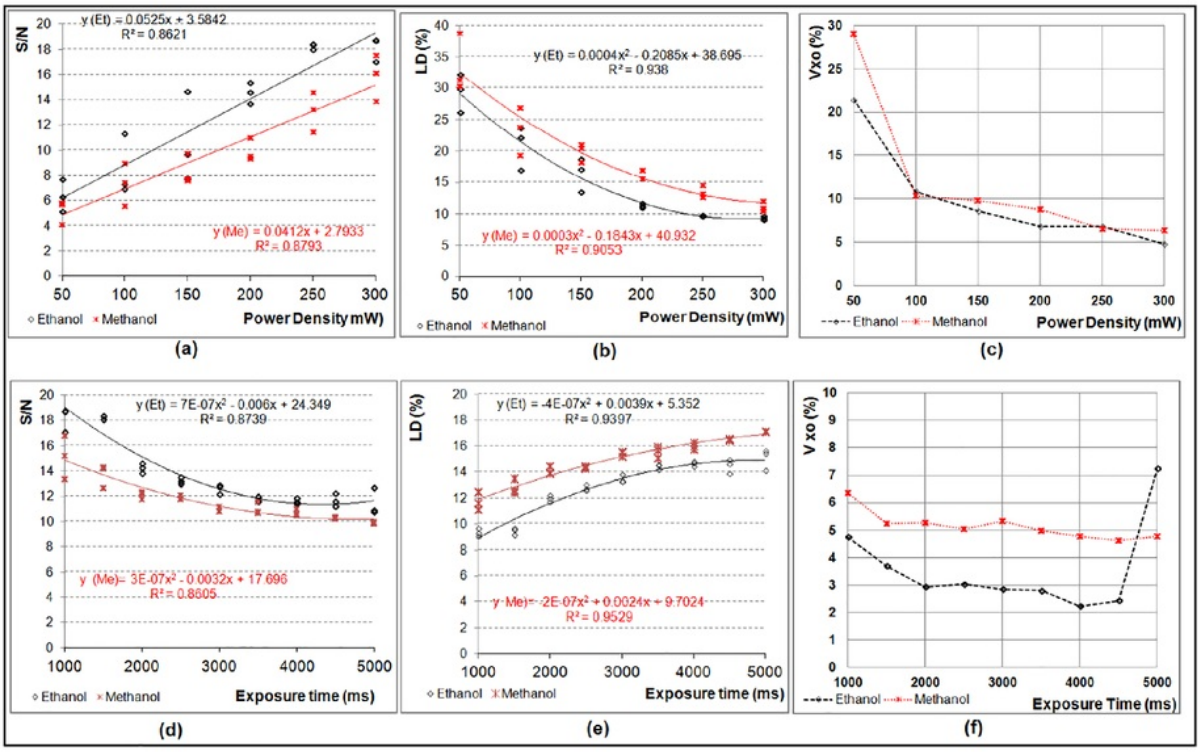

Fig. 5. The influence of power laser and exposure time on the sensitivity and precision of Raman.

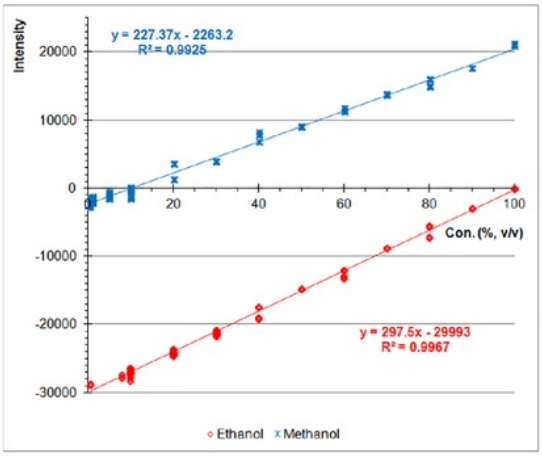

Fig. 6. The Calibration curves of both methanol and ethanol.

alcohol produced C_{correl}-values at 35% or more, and this increased along with rising methanol concentration.

3.2. The PD and ET on Raman determination test

The mean and RSD of Raman signal measurements of both solvents are presented in Fig. 4. The prolonged exposure time enhanced linearly of the Raman signal. All exposure time provided good precision measurements (RSD < 2%). Figures five a – b present the influence PD on the S/N-ratio and DL of absolute ethanol and methanol using Raman measurement. The signal of Raman spectrophotometer is a product of both PD- and ET-values [4]. An increase in PD-value enhances linearly

Table 1
The Validation parameter determinations of both methanol and ethanol.

	Ethanol	Methanol
Linear regression coefficient	0.9967	0.9925
V_{xo}	4.62	11.51
CCα (α = 5%, %, v/v)	1.2	1.9
CCβ (%, v/v)	2.3	3.8
LQ (%, v/v)	3.5	5.6

of the S/N-ratio of the Raman signal (see Fig. 5.a) and it induced a decrease in the DL of both solutes. The DL-values on the PD of 50 mW ranged between 26.1% and 32.2% (v/v) for ethanol and between 30.4 and 38.9% (v/v) for methanol. Highly sensitive measurements were obtained when the PD value was set at 300 mW, and this presented DL-values of between 9.0 and 9.6% (v/v) for ethanol and between 10.6 and 12.1% (v/v) for methanol.

Fig. 5d–e shows the influence of ET variation and Fig. 5c, and f presents the measurement precision of the series solute concentrations of both ethanol and methanol. Fig. 5.f shows the optimum time to measure the Raman signal. Prolonged time measurement decreased the S/N-ratio of both pure ethanol and methanol. The extension exposure time enhanced both the signal and noise, but noise stepped-up greater than signal. This induced the escalation of the DL from 9.3 to 15.1% for ethanol and from 11.7 to 17.1% for methanol.

The calibration function of regression analysis provided a linear relationship between concentration and Raman signal. The residual standard deviation (S_y) is the scatter of measured Raman signal value around the regression line. The relative process standard deviation (V_{xo}) described the precision of measurement in all series of concentrations. The V_{xo} was calculated by dividing the S_y with the slope of the regression and the mean series of concentrations [3,10]. The measurement on PD of 50 mW provided V_{xo} of 21.5% and 29.1% for ethanol

Table 2
The Screening and determination results of ethanol-based antiseptic – disinfectants.

No	ID No	C_{correl} value			Measurement result	
		$C_{pEt\text{-}S}$	$C_{pMe\text{-}S}$	$C_{sM\text{-}sS}$	Ethanol	Methanol
1	Et-70%-B1	42.7 ± 0.32	86.0 ± 0.43	71.4 ± 0.12	8.3 ± 0.04	25.3 ± 0.27
2	Et-70%-B2	42.8 ± 0.58	85.9 ± 0.11	71.9 ± 0.17	8.8 ± 0.16	26.5 ± 0.33
3	Et-96%-B3	26.1 ± 0.17	99.6 ± 0.01	99.2 ± 0.04	nd	90.2 ± 0.49
4	Et-70%-B4	99.1 ± 0.03	25.8 ± 0.19	35.7 ± 0.79	61.9 ± 0.21	3.4 ± 0.30
5	Et-70%-B5	99.0 ± 0.09	26.2 ± 0.26	37.1 ± 0.34	61.5 ± 0.43	3.7 ± 0.44
6	Et-70%-O1	99.0 ± 0.03	26.4 ± 0.34	38.0 ± 1.38	64.5 ± 0.50	5.4 ± 1.19
7	Et-70%-O2	99.0 ± 0.02	26.7 ± 0.20	38.8 ± 0.50	64.4 ± 0.31	4.8 ± 0.35
8	Et-95%-O1	99.7 ± 0.01	26.5 ± 0.11	34.5 ± 0.83	84.2 ± 0.45	6.8 ± 0.11
9	Et-95%-O2	99.7 ± 0.01	26.4 ± 0.14	35.5 ± 0.62	84.7 ± 0.58	6.9 ± 0.52
10	Et-96%-B1	99.9 ± 0.00	27.9 ± 0.10	36.7 ± 0.89	85.2 ± 0.75	8.3 ± 0.21
11	Et-96%-B2	99.9 ± 0.06	27.3 ± 1.16	34.5 ± 2.96	85.2 ± 0.12	7.7 ± 1.42
12	Et-70%-B6	99.2 ± 0.05	25.9 ± 0.16	36.3 ± 0.40	67.6 ± 0.15	4.4 ± 0.39
13	Arak-Op1a	93.5 ± 0.49	23.6 ± 0.31	37.4 ± 0.57	23.7 ± 0.82	8.0 ± 1.15
14	Arak-Op2a	96.4 ± 0.11	23.2 ± 0.41	36.8 ± 0.56	36.8 ± 0.86	8.2 ± 1.04
15	Arak-Op3a	95.3 ± 0.29	22.9 ± 0.33	37.4 ± 0.25	31.3 ± 1.74	7.5 ± 1.75
16	Wine 1	78.5 ± 0.30	25.2 ± 0.50	35.8 ± 0.14	14.7 ± 0.10	nd
17	Wine 2	84.9 ± 0.22	27.1 ± 0.38	36.7 ± 0.16	17.5 ± 0.29	nd
19	Wine 3	83.9 ± 0.54	25.6 ± 0.24	35.9 ± 0.07	16.2 ± 0.07	nd

and methanol, respectively, and these decreased close to 5% on PD of 300 mW. Increasing in PD value governed high precision of measurement. The quantitative analysis using Raman spectrophotometer should be done at the maximum PD energy and the optimal exposure time.

Fig. 5.f describes that the PD of 300 mW and ET of 4000 ms delivered the precise and accurate determination of both methanol and ethanol content. Taking the intensity of the subtracted Raman spectra (Fig. 3.b) at 879 and 1029 cm^{-1} into account, so that the calibration curve of both ethanol and methanol could be described (see Fig. 6). Their statistic quantification parameters are presented in Table 1. This intensity subtracted peak at 1029 cm^{-1} correlated with methanol concentration, while the peak of 879 cm^{-1} was linear to ethanol concentration. The statistical quantification parameters of both ethanol and methanol are presented in Table 1. The linear regression equation – calibration curve of ethanol is Y = 227.37 ×.– 2263.2 with the regression coefficient of 0.9925 for methanol and was Y = 297.6 × – 29993, with the regression coefficient of 0.9967 for ethanol. The developed method was linear in a wide range of both methanol and ethanol concentrations (0.5–99.9%, v/v). Determination ethanol introduced the V_{xo} of 4.63%, and this indicated that the method possessed good precision to determine ethanol. Diluting media increased the height V_{xo} value of methanol. The non-aqueous media introduced higher Raman signal of methanol than aqueous. Both peaks could be utilised to determine concentration methanol and ethanol simultaneously.

3.3. Determination of ethanol and methanol contained in samples collected from market

Table 2 presented the screening and determination test results of samples. The *arak-oplosan* samples were found to contain methanol as major containment. Almost all ethanol-based antiseptic-disinfectants contained methanol as minor containment with a range of 3.4–8.3% (v/v). Ontherhand none registered wine samples were detected contained methanol

Dilution of both ethanol and methanol decreased the similarity of Raman spectra when compared to absolute ones. Their similarity-values on the limit detection (based on S/N) were 66.8 ± 1.8% and 58.1 ± 3.2% for ethanol and methanol, respectively. Based on this fact, it was found that three samples (no 1–3) possessed $C_{pEt\text{-}S}$-values of lower than 66.8% and $C_{pMe\text{-}S}$-values of more than 58.1%. This hit to guess, that the major contains samples were methanol. The $C_{sM\text{-}S}$-value guided us to decide that the major content of the antiseptic-disinfectant samples was methanol. In other cases, samples 3–15 delivered $C_{pEt\text{-}S}$-values of 93 – 99% and their $C_{pMe\text{-}S}$-values were lower than cut off the similarity of methanol. It presumed that ethanol was their major content. The $C_{sM\text{-}sS}$–values ranged from 34.5 to 38.0%. This ranged-values is possible provided by lower methanol contain (see Fig. 3.d.), and the determination test declared that the methanol content ranged from 3.4 to 8.3% (v/v). Screening test using the values of $C_{pEt\text{-}S}$, $C_{pMe\text{-}S}$, and $C_{sM\text{-}sS}$ introduced a sensitive and selective method to identify methanol content in ethanol antiseptic-disinfectants.

4. Conclusion

Increasing power laser-induced sensitive and selective methanol and ethanol identification. The optimal condition instrument setting for the screening test and determination test of methanol content in ethanol-based products was at ET of 4000 ms and PD of 300 mW. Taking the C_{correl}-values of $C_{pEt\text{-}S}$, $C_{pMe\text{-}S}$, and $C_{sM\text{-}sS}$ provided a selective and specific method to identify methanol content in ethanol-based products.

Ethics approval and consent to participate
Ethics approval is not applicable
Consent to participate is not applicable
Consent for publication
Not applicable.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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I attest to the fact that the author listed on the title page has read the manuscript, attest to the validity and legitimacy of the data and its interpretation, and agree to its submission to “Forensic Chemistry ”.

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