Detection and quantitative determination of diethylene glycol in ethyl alcohol using gamma- ray spectroscopy

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Abstract Determination of the toxic diethylene glycol contamination in ethyl alcohol demands a rapid, accurate and reliable method. Diethylene glycol (DEG) ingestion, accidental or intentional, can lead to death. Clinical and analytical methods used to detect diethylene glycol in alcohol require several hours to days due to tedious instrument handling and measurements. Enzymatic assays face difficulty due to analytical problems. As an alternative method of data analysis, we have used γ -ray spectroscopic method to estimate the diethylene glycol contamination in alcohol by monitoring the variation in the linear and mass attenuation coefficients. This method is simple, robust, portable and can provide reliable and quantitative information about the ethyl alcohol adulterated with diethylene glycol which is of broader interest to society.

Keywords Diethylene glycol · Ethyl alcohol · Adulteration · Detection · Gamma-ray spectroscopy

Introduction

Diethylene glycol (DEG) is a colorless, odorless, hygroscopic solvent, soluble in water and ethanol (Marraffa 2014). Diethylene glycol is used in the manufacture of resins, plasticizers, morpholin etc. and as a solvent in the synthesis of nitrocellulose, organic compounds, skin screen, deodorants

and lotions. It is also used as a coolant, lubricant, brake fluid, artificial fog and antifreeze (O'Neil 2006). Expensive wines are often adulterated with the addition of fruit juices, toxic chemicals such as methanol, lead acetate to induce sweetness, cinnamon and ginger to compensate for color and flavor (van der Linden-Cremers and Sangster 1985; Molotsky, 1985). Depending on the level of consumption of toxic adulterant, the toxicity level will be graded (Schep et al., 2009; Ferrari 2005; Megarbane et al., 2005). Diethylene glycol is orally ingested accidentally or intentionally is readily absorbed through the gastro intentional tract and distributed in the blood stream throughout the body and the concentration reaches peak in 2 h (IPCS., 2001; Marraffa et al. 2008). The lethal dose of diethylene glycol is estimated to be 100 mL/kg. Liver will be able to metabolize 80 % of the absorbed diethylene glycol and broken down into oxalic acid as an end product using alcohol dehydrogenase enzymes. Oxalic acid will then react with calcium content in the blood to form calcium oxalate which gets deposited in the tissues and renal tubes of kidney and brain thus inhibiting the electron transport chain (Ballantyne et al. 2005; Hanif et al. 1995; Victor et al., 1998). There are other effects such as CNS manifestations, ocular paresis, myoclonus, seizures, somnolence, disorientation, agitation, euphoria. Diethylene glycol also increases serum osmolarity with osmolar gap, serum creatinine concentration, oliguria, hypertension, cardiac dysrhythmia, hyperkalemia, hyponatremia, progressive lethargy, facial paralysis, dysphonia and coma leading to death (Hovda et al., 2004; Hovda et al., 2004).

The most commonly used analytical methods for the detection and quantification of diethylene glycol are based on gas chromatography coupled to flame ionization detection (FID) or mass spectrometric detectors (Felder et al., 1980; Ballarin 1980; Castle et al., 1988; Maurer and Kessler 1988; Shin et al., 2008; Williams et al., 2000; William et al. 2010;

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JoEtta et al. 2011). There are reports on the use of (Livesey et al. 1995; JoEtta et al. 2011; Hague Health Council report, 2007) of GC method to determine many alcohols and diols of clinical interest without interference. Colorimetric and enzymatic methods and automated chemical analyzers could be potentially adapted for use at the point of care.

Analysis of ethyl alcohol adulterated with diethylene glycol is difficult and also most of the analytical methods mentioned are destructive to the samples. Diethylene glycol generally requires manipulation of the sample by derivatization prior to its estimation in majority of clinical laboratories and also need to obtain an assay for the determination of diethylene glycol levels (Bonn, 1985; Eder et al. 1998; Juenke et al., 2011). γ -ray spectroscopy is generally used in nuclear science research. Interaction of γ -ray radiation with solids/solutions/gases can provide significant information about the chemical constituents present in the sample. The photon-attenuation coefficient and mass absorption coefficient depends on the energy of the incident γ -ray radiation and the chemical composition of the sample (Hubbel and Seltzer, 1982). The linear attenuation coefficients of KCl, NH_4Cl , FeSO_4 , CoSO_4 , carbohydrates, phenol, nitroaniline, urea and lactose in milk at different concentrations have been reported using γ -ray spectroscopic technique (Gerward 1996; Teli and Chaudhari 1996; Teli 1998; Chaudhari and Nathuram 2010; Chaudhari and Rathod 2013; Mitkar and Dongarge 2012; Mudahar et al., 1991). We have recently reported the detection and quantitative estimation of melamine content in milk powder using γ -ray spectroscopy (Udagani and Ramesh 2014). Till date there are no reports on the application of γ -ray spectroscopy to determine the diethylene glycol adulteration in alcohol. The linear attenuation coefficients of diethylene glycol, ethyl alcohol and the mixture of diethylene glycol and ethyl alcohol was measured using γ -ray spectroscopy. The linear attenuation coefficient increases with increase in the quantity of diethylene glycol in alcohol. The technique used is non-destructive, handy and portable in nature which has an advantage over other methods.

Experimental work

Materials and methods

Diethylene glycol and ethyl alcohol were procured from SD Fine Chemicals, India and used without purification.

Calibration

The preliminary experiments were carried out to determine stability and linearity of the γ -ray spectrometer.

The energy resolution of the γ -ray spectrometer was found to be 6 % at 0.662 MeV. Experiments were carried out to measure the linear attenuation coefficients of diethylene glycol and ethyl alcohol separately to obtain the standard curves.

Sample analyses

Diethylene glycol-ethyl alcohol mixtures were taken at different volume ratio and heights and their linear attenuation coefficients were measured.

Theory

The intensity of γ -ray radiation after transmission through the sample of thickness 'x' is:

$$I = I_0 e^{(-\mu x)}$$

Where ' I_0 ' and ' I ' are initial and final intensities of γ -ray radiation and ' μ ' is the linear attenuation coefficient of the sample. The above equation is modified i.e., $I = I_0 e^{-\mu h}$ where ' I ' is the intensity of γ -radiation after traversing the height ' h ' of chemical solution. Using the density (ρ) and linear attenuation coefficient (μ) values, information about the mass attenuation coefficient (μ/ρ) can be evaluated. For chemical mixtures, the total mass attenuation coefficient (μ/ρ) is related to the (μ/ρ) values of each constituent component. The total mass attenuation coefficient (μ/ρ) of chemical solution can be calculated by using the mixture rule

$$\frac{\mu}{\rho} = w_i \left(\frac{\mu}{\rho} \right)_i$$

Where ' w_i ' is the weight fraction of the i^{th} constituent. If we mix diethylene glycol in ethyl alcohol, homogeneous solution

Fig. 1 Experimental arrangement

Table 1 Spectral analysis for pure ethyl alcohol

Thickness (cm)	Counts under ROI	Counts per sec	$\ln \frac{I}{I_0}$	Mean linear attenuation coefficient (cm ⁻¹)	Attenuation coefficient (cm ⁻¹) by graph
0	24,425	244.25	—	0.0677	0.06821±5.5278×10 ⁻⁴
1	22,837	228.37	0.0674		
2	21,381	213.81	0.1336		
3	19,897	198.77	0.2054		
4	18,592	185.92	0.2729		
5	17,387	173.87	0.3388		

is formed. For homogeneous solution, linear attenuation coefficient can be calculated theoretically using the relation

$$\mu_{\text{theory}} = W_{\text{diethyleneglycol}} \times \mu_{\text{diethyleneglycol}} + W_{\text{ethylalcohol}} \times \mu_{\text{ethylalcohol}}$$

where $W_{\text{Diethylene glycol}}$ is the percentage composition of diethylene glycol by weight, $W_{\text{ethyl alcohol}}$ is the percentage composition of ethyl alcohol by weight, $\mu_{\text{Diethylene glycol}}$ represents the linear attenuation coefficient of diethylene glycol and $\mu_{\text{ethyl alcohol}}$ is linear attenuation coefficient of ethyl alcohol.

The GSpec γ -ray spectrometry system consists of NaI (TI) crystal detector of size 2"x2" and multichannel analyzer (MCA). Spectrum Acquisition and Analysis Software (SAAS) was used for data acquisition and control during the experiment. The calibration of energies was carried out using Co-60 (1.17, 1.33 MeV) and Cs-137 (0.66 MeV).

The concentration of a solution can be defined as amount of solute dissolved in the solvent. Concentration can be expressed using i) percent composition, ii) w/w%, iii) v/v%, iv) normality, v) molarity, vi) molality. The concentration in terms of percent composition by volume and the percent composition by weight are described.

The percent composition by v/v (%) of the solute by the total volume of the solution is given by

$$\text{Percent composition by volume (\%)} = \frac{\text{volume of solute}}{\text{volume of the solution}} \times 100$$

Variable parameters to estimate linear and mass attenuation coefficients

The variation in the linear attenuation coefficient by mixing the varying percent composition by volume (%) of diethylene glycol in ethyl alcohol was examined. The linear attenuation coefficients of ethyl alcohol, diethylene glycol, 20, 27.27, 33.33 and 38.46 % composition by volume of diethylene glycol in ethyl alcohol was recorded.

80 mL ethyl alcohol was taken in a measuring cylinder and 20 mL of diethylene glycol was added to it, to prepare 20%v/v of diethylene glycol in ethyl alcohol. To prevent the evaporation of the ethyl alcohol in the solution, top of the cylinder was gently wrapped with para film. The glass cylinder was gently invert several times until the ethyl alcohol and diethylene glycol is mixed homogeneously. The 27, 33.33 and 38.46 % solutions were prepared using the above procedure.

The γ -ray spectrometry was tested for resolution, linearity and stability characteristics. The resolution of the detector was 6 % for 0.662 MeV γ -rays at 750 V. The schematic representation of the experimental setup is shown in Fig. 1. The ¹³⁷Cs radioactive source was placed in line with the γ -ray spectrometer assembly and the spectrum of γ -rays without sample was acquired for 100 s. The Region of Interest (ROI) and peak were selected. The SAAS provides integral counts, background counts and difference between the integral and background counts under ROI. For fixed experimental geometry, the photopeak appears at 0.662 MeV when ¹³⁷Cs radioactive source was used. Using the above experimental

Table 2 Spectral analysis for pure diethylene glycol

Thickness (cm)	Counts under ROI	Counts per sec	$\ln \frac{I}{I_0}$	Mean linear attenuation coefficient (cm ⁻¹)	Attenuation coefficient (cm ⁻¹) by graph
0	25,617	256.17	—	0.0981	0.0967±4.9369×10 ⁻⁴
1	23,196	231.96	0.0993		
2	21,015	210.15	0.1980		
3	19,130	191.30	0.2919		
4	17,316	173.16	0.3916		
5	15,754	157.54	0.4860		

setup, empty glass beaker was mounted directly in line with the ^{137}Cs radioactive source and detector at opening end of the safety wooden box and the number of counts under ROI was recorded for 100 s (see Table 1). Ethyl alcohol was filled into the glass beaker to a height of 1 cm. With the same detector-source geometry the counts under ROI was noted for 100 s for ethyl alcohol.

The experiment was repeated with different height of ethyl alcohol. The same procedure was employed for the determination of attenuation coefficients of diethylene glycol and different concentrations of ethyl alcohol-diethylene glycol solution mixtures and the values are tabulated in Tables 2 and 3. Diethylene glycol, ethanol and the mixtures of diethylene glycol-ethanol (circles) exhibits a linear increase over height.

Fig. 2 Plot of $\ln(I_0/I)$ versus thickness for ethyl alcohol

Results and discussion

Adulteration of food and beverages using cheaper and harmful substituents is a major problem faced by the humanity. Mixing cheaper solvent i.e. diethylene glycol in alcohol based beverages to induce sweetness and reduce the cost has caused thousands of death each year (Risk Assessment studies, 2003; Spink 2014). The

analytical techniques used to detect such adulterants is not fool proof hence it is essential to explore the validity of the reported methods and use alternative and non-destructive technique which is free from the usage of other reagents to detect qualitatively as well as quantitatively the presence of diethylene glycol in ethyl alcohol.

Table 3 Spectral analysis for varying % composition by volume of diethylene glycol in ethyl alcohol

% of Diethylene glycol	Thickness (cm)	$\frac{I_0}{I}$	$\ln \frac{I_0}{I}$	Linear attenuation coefficient (cm^{-1})	Linear attenuation coefficient (cm^{-1}) by mixture rule
0	1	1.0697	0.0674	0.0677	0.0677
	2	1.1429	0.1336		
	3	1.2280	0.2054		
	4	1.3138	0.2729		
20	1	1.0768	0.0740	0.0736	0.0738
	2	1.1589	0.1474		
	3	1.2452	0.2193		
	4	1.3425	0.2946		
27.27	1	1.0773	0.0744	0.0755	0.0760
	2	1.1626	0.1506		
	3	1.2558	0.2277		
	4	1.3568	0.3052		
33.33	1	1.0806	0.0775	0.0778	0.0778
	2	1.1690	0.1562		
	3	1.2611	0.2320		
	4	1.3670	0.3126		
38.46	1	1.0822	0.0790	0.0787	0.0794
	2	1.1717	0.1585		
	3	1.2630	0.2335		
	4	1.3701	0.3149		

Linear attenuation coefficient

The densities of ethyl alcohol and diethylene glycol are 0.789 and 1.12 g cm^{-3} respectively. Presence of diethylene glycol in ethyl alcohol results in the variation in the bulk density of ethyl alcohol. This variation will affect the linear attenuation coefficient of ethyl alcohol and has been measured using γ -ray spectroscopy effectively.

Accuracy and linearity

Figures 2 and 3 show the plots of $\ln(I_0/I)$ vs path length (*i.e.* thickness in cm) for ethyl alcohol and diethylene glycol separately using the spectral analyses data shown in Tables 1 and 2. The linearity of the data for diethylene glycol and ethyl alcohol were evaluated by varying different heights of ethyl alcohol and diethylene glycol respectively. Figures 1 and 2 show the linearity and accuracy determined using linear regression equation *i.e.* $y = -0.0010 + 0.06821x$; $r = 0.9999 \pm 0.0017$ for ethyl alcohol and $y = -0.00326 + 0.0967x$; $r = 0.9999 \pm 0.00156$ for diethylene glycol respectively.

The Table 3 shows the spectral analysis data for diethylene glycol-ethyl alcohol mixture. The experimental data are fitted by the least square method. Linearity was assessed for diethylene glycol/ethyl alcohol over different heights of 1–5 cm. Figure 4 shows the variation of linear attenuation coefficient of diethylene glycol-ethyl alcohol mixture with varying percentage composition by volume of diethylene glycol in ethyl alcohol; the linear attenuation coefficient of diethylene glycol-ethyl alcohol mixture varies linearly with

Fig. 3 Plot of $\ln(I_0/I)$ versus thickness for Diethylene glycol

Fig. 4 Variation of linear attenuation coefficient with varying % composition by volume of Diethylene glycol in ethyl alcohol

varying %composition by volume of diethylene glycol. The linear and mass attenuation coefficients increase with an increase in the presence of diethylene glycol in ethyl alcohol (see Fig. 4). The energy resolution of NaI (TI) detector is usually 6 % at 0.662 MeV gamma rays. The detector can be used to carry out experiments even at lower weight ratios of diethylene glycol and ethyl alcohol. The densities of diethylene glycol and ethyl alcohol and their mixtures are different. Hence to observe the significant changes in the density of bulk ethyl alcohol where diethylene glycol is present we have used 20 wt% of diethylene glycol. This does not indicate the limitation of the technique.

Conclusion

The study of linear attenuation coefficients of ethyl alcohol, diethylene glycol and solution containing diethylene glycol in ethyl alcohol using γ -radiation energy of 0.662 MeV explores the validity of the linearity in pure diethylene glycol and ethyl alcohol. The differences in the densities of standard solvents such as ethyl alcohol, diethylene glycol and the diethylene glycol adulterated ethyl alcohol affect the linear attenuation coefficient values. The article provides an alternative technique for the determination toxic chemical constituents used to adulterated ethyl alcohol. The proposed γ -ray spectroscopic technique is one of the potential tool which can provide real-time quantitative information about the presence of diethylene glycol in ethyl alcohol at lower cost and can be used for routine monitoring of diethylene glycol in ethyl alcohol.

References

- Ballantyne B, William M, Snellings WM (2005) Developmental toxicity study with diethylene glycol dosed by gavage to CD rats and CD-1 mice. *Food Chem Toxicol* 43:1637–1646
- Ballarin C (1980) Studies on the identification of pharmacopeial glycols by thin-layer chromatography. *Pharm Prax* 35260–35264
- Bonn G (1985) High-performance liquid chromatography of carbohydrates, alcohols and diethylene glycol on ion-exchange resins. *J Chromatogr A* 350:381–387
- Castle L, Cloke HR, Jr S-t (1988) Gas chromatographic determination of monoethylene glycol and diethylene glycol in chocolate packaged in regenerated cellulose film. *J Assoc Anal Chem* 7:499–502
- Chaudhari LM, Nathuram R (2010) Absorption coefficient of polymers (Polyvinyl Alcohol) by using gamma energy of 0.39 MeV. *Bulg J Phys* 38:232–240
- Chaudhari LM, Rathod SZ (2013) Measurement of attenuation coefficient of glucose solution. *J Chem Bio Phy Sci* 3:2086–2091
- Diethylene glycol health-based recommended occupational exposure limit, the Hague health council of the Neatherlands, 2007, publication no. 2007/03OSH
- Eder AF, McGrath CM, Dowdy YG, Tomaszewski JE, Rosenberg FM, Wilson RB, Wolf BA, Shaw LM (1998) Ethylene glycol poisoning: toxicokinetic and analytical factors affecting laboratory diagnosis. *Clin Chem* 44:168–177
- Felver ME, Lakshmanan MR, Wolf S (1980) The presence of 2,3-butanediol in the blood of chronic alcoholics admitted to an alcoholic treatment center. *Adv Exp Med Biol* 132:229–235
- Ferrari LA, Giannuzzi L (2005) Clinical parameters, postmortem analysis and estimation of lethal dose in victims of a massive intoxication with diethylene glycol. *Forensic Sci Int* 153:49–51
- Gerward L (1996) On the attenuation of X-rays and gamma rays in dilute solutions. *Radiat Phys Chem* 48:697–826
- Hanif M, Mobarak MR, Ronan A, Rahman D, Donovan JJ, Bennish ML (1995) Fatal renal failure caused by diethylene glycol in paracetamol elixir: the Bangladesh epidemic. *Biochem Med J* 311:88–91
- Hovda KE, Hunderi OH, Rudberg N, Froyshov S, Jacobsen D (2004) Anion and osmolal gaps in the diagnosis of methanol poisoning: clinical study in 28 patients. *Intensive Care Med* 30:1842–1846
- Hubbel JH, Seltzer SM (1982) Tables of X-ray mass attenuation coefficients and mass energy-absorption coefficients from 1 keV to 20 MeV for elements $Z = 1$ to 92 and 48 additional substances of dosimetric interest. *Int J Appl Radiat Isot* 33:126
- JoEtta MJ, Lindsay H, Gwendolyn AM, Gary LH (2011) Rapid and specific quantification of ethylene glycol levels. *Am J Clin Pathol* 136:318–324
- Juenke JM, Hardy L, McMillin GA, Horowitz GL (2011) Rapid and specific quantification of ethylene glycol levels-adaptation of a commercial enzymatic assay to automated chemistry analyzers. *Am J Clin Pathol* 136:318–324
- Livesey JF, Perkins SL, Tokessy NE, Maddock MJ (1995) Simultaneous determination of alcohols and ethylene glycol in serum by packed- or capillary-column gas chromatography. *Clin Chem* 41:300–305
- Marraffa JM (2014) Diethylene glycol, encyclopedia of toxicology (Third Edition), 140–142
- Marraffa JM, Holland MG, Stork CM, Hoy CD, Hodgman MJ (2008) Diethylene Glycol: widely used solvent presents serious poisoning potential. *J Emerg Med* 35:401–406
- Maurer H, Kessler C (1988) Identification and quantification of ethylene glycol and diethylene glycol in plasma using gas chromatography–mass spectrometry. *Arch Toxicol* 62:66–69
- Megarbane B, Borron SW, Baud FJ (2005) Current recommendations for treatment of severe toxic alcohol poisonings. *Intensive Care Med* 31:189–195
- Mitkar SR, Dongarge SM (2012) Measurement of linear and mass attenuation coefficient of alcohol soluble compound for gamma rays at energy 0.511 MeV. *Arch Appl Sc Res* 4:1748–1752
- Molotsky I (1985) Popular wines found to hold toxic chemical. *The New York Times*, November 1, Retrieved May 8:2014
- Mudahar GS, Modi S, Singh M (1991) Total and partial mass attenuation coefficients of soil as a function of chemical composition. *Appl Radiat Isot* 42:13–18
- O’Neil M (2006) The merck index, 14th edn. Merck & Co., Whitehouse Station
- International Programme on Chemical Safety (IPCS) (2001) Ethylene glycol. Poisons information monograph. PIM 227
- Risk assessment studies report No. 15, (November 2003). Chemical hazard evaluation, risk assessment on artificial sweeteners in beverages, food and environmental hygiene department, HK SAR, Risk Assessment Section, Food and Environmental Hygiene Department 43/F, Queensway Government Offices, 66 Queensway, Hong Kong
- Schep LJ, Slaughter RJ, Temple WA, Beasley DMG (2009) Diethylene glycol poisoning. *Clin Toxicol* 47:525–535
- Shin JM, Sachs G, Jeffrey AK (2008) Simple diagnostic tests to detect toxic alcohol intoxications. *Transl Res* 152:194–201
- Spink J (2014) Safety of food and beverages: risks of food adulteration. *Encycl Food Saf* 3:413–416
- Teli MT (1998) On the attenuation of X-rays and gamma rays for aqueous solutions of salts. *Radiat Phys Chem* 53:593–595
- Teli MT, Chaudhari LM (1996) Linear attenuation coefficient of gamma radiation in dilute solutions of potassium chloride. *Appl Radiat Isot* 47:365–367
- Udagani C, Ramesh TN (2014) Quantitative detection of melamine adulteration in milk powder using g-ray spectroscopic technique. *Int J Res Appl Nat Soc Sci* 2:81–88
- van der Linden-Cremers PM, Sangster B (1985) Medical sequelae of the contamination of wine with diethylene glycol. *Ned Tijdschr Geneesk* 129:1890–1891
- Victor PS, Espindola J, Needham LL, Denerville K (1998) Epidemic of pediatric deaths from acute renal failure caused by diethylene glycol poisoning. *J Am Med Assoc* 279:1175–80
- William HP, Philip W, Rutter (2010) Improved GC-MS procedure for simultaneous measurement of ethylene glycol and glycolic acid. *Clin Chem* 56:1900
- Williams RH, Shah SM, Maggiore JA, Erickson TB (2000) Simultaneous detection and quantization of diethylene glycol, ethylene glycol, and the toxic alcohols in serum using capillary column gas chromatography. *J Anal Toxicol* 24:621–626