SELECTIVE TRACE LEVEL DETERMINATION OF 1,4-DIOXANE CONTENT IN SODIUM LAURETH SULFATE RAW MATERIAL BY GAS CHROMATOGRAPHIC-FLAME IONIZATION DETECTION METHOD

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ABSTRACT

Objective: The study spotlights on a new gas chromatographic (GC) method with flame ionization detection technique that has been developed and validated for the selective determination of 1,4-dioxane content in sodium laureth sulfate (SLS) raw material.

Methods: The method was developed using a Thermo Scientific TR-1 (30 m×0.25 mm×1.0 μm) column with a carrier gas used as helium. The diluent used as purified water and the flow pressure of the carrier gas is 9.0 psi with a split ratio of 1:5. The optimized method was validated as per the ICH Q2 guidelines.

Results: Regression analysis confers a correlation coefficient for the stated compounds that are found to be greater than 0.999. The limit of quantitation and limit of detection are established at a sensitive determination level of 9 ppm and 3 ppm, respectively.

Conclusion: The validated and rugged GC method developed for the determination of 1,4-dioxane using a specific GC method in the SLS raw material. The recovery results prove the sound judgment in the determination of accuracy toward its evaluation. Hence, the validated analytical method was specific, selective, economical, and accurate for the determination of 1,4-dioxane by gas chromatographic method with flame ionization detection technique.

Keywords: 1,4-Dioxane, Sodium laureth sulfate, Raw material, Gas chromatographic with flame ionization detection, Trace level determination.

INTRODUCTION

The appearance of sodium laureth sulfate (SLS/SDS) raw material has the Flowable paste/powder and transparent to yellowish color. SLS is the key material for the manufacture of liquid dishwashing and technical agents as well as liquid light duty-detergents. Because of its excellent foam characteristic and the natural thickening with salt, the product is also suited as a primary surfactant for cosmetic cleansing preparation such as shampoo, shower gel, and foam baths. Sodium lauryl ether sulfate derived from natural fatty alcohols.

The purification process of the SLS raw material eliminates most of the components, namely, sodium chloride, sodium sulfate, and 1,4-dioxane and unsulfated alcohol. However, the quantitation levels shall be determined using the selective analytical methodology for 1,4-dioxane impurity. The literature describes few methods on the determination of 1,4-dioxane using specific variable instrumentation techniques such as gas chromatographic (GC) with flame ionization detection (FID), GC with mass detection on a variety of raw materials, namely, fatty oil alcohols [1,2], polysorbates [3], ethoxylated surfactants [4-6], and few of them were reported in finished product cosmetic applications [7-11]. There were several other kinds of literature sourced as the major contaminant in water [12,13] and listed as environmentally hazardous [14] and possible risk assessments in terms of carcinogenicity [15] and household detergent and personal care products [16] were also reported. No instrumental analysis was reported for 1,4-dioxane determination and none of the methods found relevant either in the similar sample matrix. Hence, a method was developed and validated to determine the 1,4-dioxane (as a contaminant impurity) by gas chromatography with flame ionization technique to evaluate the quality and purity of the SLS, raw material.

EXPERIMENTAL

Chemicals and types of equipment

The purity of 1,4-dioxane used as analytical grade (>95%) in chromatographic development. Purified water prepared using a Milli-Q Plus water purification system (Millipore, Milford, MA, USA). GC column

Table 1: Gas chromatograph and headspace conditions

| GC oven conditions |
|-------------------|
| **Initial temperature:** 70.0°C |
| **Initial time:** 0.0 min |

| Ramp# | Rate (°C/min) | Final temperature (°C) | Hold time (min) | Total time (min) |
|-------|---------------|------------------------|----------------|-----------------|
| 1 | 12.0 | 190 | 0.00 | 10.00 |
| 2 | 30.0 | 220 | 19.00 | 30.00 |

Run time : 30.00 min

Oven equilibration time: 0.00 min

Headspace autosampler conditions

| Headspace autosampler conditions |
|----------------------------------|
| **Oven temperature:** 90°C |
| **Loop temperature:** 120°C |
| **Transfer line temperature:** 130°C |
| **GC cycle time:** 60 min |
| **Vial equilibration time:** 30.0 min |
| **Fill mode:** Fill at flow to pressure |
| **Fill pressure:** 15 psi |
| **Fill flow:** 50 mL/min |
| **Loop volume:** 1 mL |
| **Pressure equilibration:** 3.00 min |
| **Vial shake mode:** 9 (high) |
| **Inject time:** 0.3 min |
obtained from Thermo Fisher Scientific Inc., USA. The chromatography technique developed in Agilent Gas Chromatograph (model 6890N) with headspace sampler (7697A) and FID equipped with waters empower software.

Chromatographic conditions
The method was developed using a Thermo Scientific TR-1 (30 m×0.25 mm×1.0 μm) column with a carrier gas used as helium. The diluent used as purified water and the flow pressure of the carrier gas is 9.0 psi with a split ratio of 1:5. The inlet and detector temperatures are maintained at 130°C and 300°C, respectively. The fuel and oxidizer flow rates maintained at 1:10 with a constant makeup gas of nitrogen with a flow rate of 25 mL/min operated with FID. The total chromatographic run time of 25 min. The gas chromatograph column oven conditions and headspace conditions are presented in Table 1.

Working standard preparation
Accurately weigh about 300 mg of 1,4-dioxane standard into respective 100 mL volumetric flask contained 20 mL of purified water. Dilute to volume with purified water and mix well. Pipette 10.0 mL of stock standard solution into 100 mL volumetric flask and dilute to volume with purified water and mix well. Pipette 2.0 mL of above solution into 100 mL volumetric flask and dilute to volume with purified water and mix well. Transfer 5.0 mL of intermediate stock standard preparation into 20 mL headspace vial and seal the vial for analysis. The concentration of 1,4-dioxane is equivalent to 30 ppm with respect to sample concentration. The system suitability of the chromatographic analysis is presented in Table 2. The representative chromatograms of the blank and working standard preparation are shown in Figs. 1 and 2.
Sample preparation
Accurately weigh about 1.0 g of SLS raw material into 20 mL headspace vial, add 5.0 mL of purified water to the headspace vial and seal the vial for analysis. The chromatogram of the control sample is shown in Fig. 3.

RESULTS AND DISCUSSION
The proposed method validated as per the ICH guidelines [17] and USP Compendia [18] along with the references literature on method validation [19-28] studies in current industry practices.

Method precision
Method precision/repeatability was determined for SLS raw material by analyzing six sample preparations of raw material spiked with 1,4-dioxane at specification level (30 ppm). A control sample was prepared to correct the recovery with a known amount of 1,4-dioxane detected in the control sample. The results for method precision are presented in Table 3. The representative chromatogram of the control sample and spiked sample (at specification 30 ppm) is presented in Figs. 3 and 4.

Fig. 3: Control sample chromatogram

Fig. 4: Spiked sample chromatogram
Fig. 5: Limit of quantitation chromatogram

Table 2: System suitability information

| Component   | Retention time (min) | Relative retention time | System suitability criteria | USP | % RSD† |
|-------------|----------------------|-------------------------|-----------------------------|-----|--------|
| 1,4-Dioxane | 1.7                  | 0.06                    | NMT 1.5 | NMT 10.0 |

†Determined on multiple sample preparations

Table 3: Method precision and accuracy evaluation

| % Level          | 1,4-dioxane – % recovery | Average | % RSD† |
|------------------|--------------------------|---------|--------|
| Limit of quantitation (~9 ppm) | 100.2 | 15.7 |
| 100% (~30 ppm)   | 84.9 | 1.8 |
| 125% (~37.5 ppm) | 100.5 | 3.0 |

†Determined on multiple sample preparations

Specificity

The specificity of the method was demonstrated by injecting blank, working standard, control, and spiked sample at specification level (30 ppm). No significant interference was observed at the retention time of 1,4-dioxane from diluent. The results for specificity are presented in Table 3 and representative chromatograms are presented in Figs. 1-4.
Accuracy
The accuracy was determined by spiking known concentrations of 1,4-dioxane in triplicate preparations at limit of quantitation (LOQ) and 125% level, and six sample preparations at a 100% level with respect to specification limit. A control (un-spiked) sample was prepared to correct the % recovery with a known amount of 1,4-dioxane detected in the control sample. The amount of 1,4-dioxane detected in the control sample was 0.012 µg/mL. The obtained recoveries are presented in Table 3.

Limits of detection (LOD) and LOQ
LOQ was established by making serial dilutions of standard solution to obtain a concentration of about 9 µg/mL. Representative chromatograms of the LOQ and LOD solutions are presented in Figs. 5 and 6.

Linearity
The linearity of the method was demonstrated by injecting series of standard solutions of 1,4-dioxane at five different concentration levels ranging from LOQ 9 ppm to 50 ppm-level. The correlation coefficient for 1,4-dioxane found to be 0.9992.

Stability of mobile phase and solutions
The solution stability was established for working standard and control sample solution which are found to be stable for 72 h at room temperature condition.

CONCLUSION
The validated and rugged GC method developed for the determination of 1,4-dioxane using a specific GC method in the SLS raw material. The recovery results prove the sound judgment in the determination of accuracy toward its evaluation. Hence, the validated analytical method was specific, selective, economical, and accurate for the determination of 1,4-dioxane by GC method with FID technique.

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CONFLICTS OF INTEREST
The author confirms that this article content has no conflicts of interest.

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