

DETERMINATION OF ALLYL ISOTHIOCYANATE & FORMULA DERIVATION

INTRODUCTION: *Allyl Isothiocyanate present in mustard oil is also known as Pungency with chemical formula as $\text{CH}_2=\text{CH}=\text{CH}_2-\text{N}=\text{C}=\text{S}$ and molecular weight 99.18g/mole. To test AITC is very sensitive as it's conc. is very low and is volatile at room temperature (flash pt 46). It is insoluble in water but good soluble in ethanol. This AITC or pungency test is important to distinguish between expeller oil or cold pressed oil.*

METHODOLOGY: *The Allyl Isothiocyanate in oil is transferred by steam distillation into a measuring flask containing excess of known silver nitrate solution where the reactions between takes place. The remaining unused AgNO_3 is calculated by titrating with standard solution of ammonium thiocyanate and similarly a blank titration is performed to find the actual total AgNO_3 taken. After finding the value of used silver nitrate and its relation with wt. of AITC, we will derive a formula to calculate the Allyl Isothiocyanate% related to titration values .*

APPARATUS & EQUIPMENTS :

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|---------------------------------|------------------------------|
| 1. Distillation flask 500ML. | 7. Measuring flask 250 ML |
| 2. Weighing balance. | 8. Water bath. |
| 3. 100ml beaker with dropper | 9. 50ml Burette with stand |
| 4. Reflux air condenser. | 10. 25ml Pipette with filler |
| 5. Steam generator. | 11. 500ml titration flasks-2 |
| 6. Long reflux water condenser. | 12. Funnel with filter paper |

CHEMICALS & REAGENTS

- | | |
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| 1. Ethyl alcohol | 4. 10% NH_4OH solution |
| 2. $\text{N}_1=\text{N}/20$ AgNO_3 solution | 5. Conc. Nitric acid |
| 3. $\text{N}_2=\text{N}/20$ NH_4SCN solution | 6. 10% Ferric ammonium sulphate |

PROCEDURE STEPS : To better understand we have divided the complete procedure of Allyl Isothiocyanate determination into following 6 steps:-

- 1. CHEMICAL & REAGENTS PREPARATION**
- 2. SAMPLE & BLANK PREPARATION**
- 3. STEAM DISTILLATION**
- 4. FILTRATION**
- 5. FORMULATION**
- 6. TITRATION (Sample & blank)**



STEP 1 CHEMICAL & REAGENTS PREPARATION

- **Ethyl alcohol** ➡ As the ethyl alcohol becomes acidic timely therefore neutralise it with N/10 NaOH solution using phenolphthalein as indicator
- **$N_1 = N/20$ AgNO₃** ➡ dissolve 4.247 g of AR grade silver nitrate in 500 ML of distilled water and standardise with NaCl solution using potassium chromate as indicator to find the actual normality
- **$N_2 = N/20$ NH₄SCN** ➡ Dissolve 1.962 g of AR grade ammonium thiocyanate in 500 ML of distilled water and standardise with N/20 AgNO₃ solution
- **10% Ferric alum as indicator** ➡ dissolve 10 g of ammonium ferric sulphate in 100ml of distilled water

STEP 2 SAMPLE & BLANK PREPARATION

Sample preparation ➡ we will weight accurately near about 5g of oil in distillation flask by mixing the sample thoroughly. If direct weighing of oil in distillation flask on the balance is not possible due the over weight of distillation flask then use the indirect method. For that take approximately 50ml of the oil in the 100ml beaker and weight it along with the dropper and note the reading W1. Now carefully transfer about 5g of oil from the beaker to the distillation flask using this dropper and again take the weight of oil beaker along with used dropper and note this as final reading W2. By subtracting final reading from the initial reading we will have the accurate weight of oil taken in the distillation flask. Now add to it 25ml of ethyl alcohol to dissolve all the AITC present in the oil and then add 150ml of distilled water. Close the distillation flask with glass stopper as the compound AITC is volatile at room temperature.

Blank preparation ➡ Take 500ml empty conical titration flask and add to it exactly 25ml of N/20 AgNO₃ solution (as same as that we will take in measuring flask for sample) and 150ml of distilled water.

STEP 3 STEAM DISTILLATION

In this process we will connect the distillation flask on one side with steam generator and on other side with long reflux water condenser using the glass joint assembly as shown in the above picture. Now we will take a 250ml of measuring flask and after adding to it exactly 25ml N/20 AgNO₃ solution and 10ml of 10% ammonium hydroxide solution, connect to the lower end of condenser. The steam generated passes through the side hole to the distillation flask and the mixture starts boiling. The vapours of AITC formed get condensed through the condenser and are collected as droplets into the measuring flask containing AgNO₃ solution and NH₄OH solution where the reaction between takes place. After collecting about 150ml of the distillate stop the distillation process and immediately remove the measuring closing with stopper.

Now either keep this measuring flask in a dark cool place overnight to have complete reaction between the chemicals or heat on a water bath by attaching the reflux air condenser for 1hour to accelerate the reaction. Cool down the mixture distillate to room temperature by keeping the measuring flask under the running water tap.

STEP 4 FILTRATION PROCESS:

As shown below in the reactions, the AITC does not react directly with AgNO₃, initially the AITC reacts with the ammonia liberated by ammonium hydroxide to produce unstable compound THIOSINAMINE and this compound further reacts with silver nitrate to form Allyl cyanamide and silver sulfide. Now our distillate contains both the unused AgNO₃ to be measured and unwanted Ag₂S, so we will remove Silver Sulfide by filtering the complete distillate into a 500ml conical titration flask using funnel and filter paper followed by rinsing the emptied measuring flask twice with distilled water.

CHEMICAL REACTION PROCESS



Allyl Isothiocyanate Ammonia Thiosinamine



Thiosinamine Silver nitrate Allyl cyanamide Silver sulfide

STEP 5 FORMULATION : To find the value of AITC firstly we will find the relation between the wt of AITC equivalent to volume of used or reacted AgNO₃ and secondly we will find the volume of used AgNO₃ by having the value of unused AgNO₃ and actual total AgNO₃ through titration processes.



In the both reactions, 2 moles of AgNO_3 reacts with 1 moles of AITC

Therefore 1L of 1N AgNO_3 = Mol.wt. of AITC/2

Or 1000ml of 1N AgNO_3 = $99.18/2 = 49.59\text{g}$ of AITC

Or 1ml of 1N AgNO_3 = 0.04959g of AITC

Or 1ml of N_1 normality of AgNO_3 = $N_1 \times 0.04959\text{g}$ AITC

Or wt of AITC for used volume V of N_1 AgNO_3 = $N_1 \times V \times 0.04959\text{g}$

EQUATION FOR AITC in (w/v) = $0.04959 \times V \times N_1$

Now in the next step we will find the value of V and put in this equation

STEP 6 TITRATION(SAMPLE & BLANK) :

For titration process we will add standard solution of ammonium thiocyanate of normality $N_2 = N/20$ in the burette.

SAMPLE TITRATION: Take the sample titration flask containing filtered distillate and add 5ml of conc. nitric acid and few drops of indicator ferric alum. Note the initial reading on the burette and start the titration by adding titrant NH_4SCN dropwise. When the colour change from grey white to red orange stop the the titration process and note the final reading on the burette. By subtracting initial reading from the final reading we will have the volume of NH_4SCN used as V_s

Now by applying Normality equality equation $N_x V_x = N_y V_y$

Putting the values in the equation $\Rightarrow N_1 V_1 = N_2 V_s \Rightarrow V_1 = V_s \times N_2/N_1$

Vol of unused AgNO_3 $\Rightarrow V_1 = V_s \times N_2/N_1$

BLANK TITRATION: Similarly titrate the blank titration flask containing total volume of AgNO_3 and note the volume of NH_4SCN used as V_b

Now by applying Normality equality equation $N_x V_x = N_y V_y$

And putting the value in the equation $\Rightarrow N_1 V_2 = N_2 V_b$

Vol of total AgNO_3 $\Rightarrow V_2 = V_b \times N_2/N_1$

V = vol of used AgNO_3 = Vol of total AgNO_3 — Vol of unused AgNO_3

$V = V_2 - V_1 = (V_b - V_s) N_2/N_1$

Now put this value of V in the AITC equation and finally we get

Equation for Wt. of AITC = $0.04959(V_b - V_s)N_2$

Now $\text{AITC}\% = \frac{\text{wt of AITC}}{\text{wt of oil}} \times 100$

Therefore **FORMULA** for **Allyl Isothiocyanate % (w/v)** $$\text{AITC}\% = \frac{0.04959(V_b - V_s) N \times 100}{W}$$

Where :

V_b = volume of NH_4SCN used in blank titration

V_s = volume of NH_4SCN used in sample titration

N = normality of NH_4SCN

W = weight of oil used for test



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SAMPLE TITRATION PROCESS



AITC

USED

UNUSED



unused

Ammonium
Thiocyanate

Silver
Thiocyanate

Ammonium
Nitrate

BLANK TITRATION PROCESS



Total

Ammonium
Thiocyanate

Silver
Thiocyanate

Ammonium
Nitrate



(Indicator)

(Red colour free ions)

During TITRATION after complete absorption of unused AgNO_3 -then very next drop of NH_4SCN reacts with indicator ferric alum to produce orange red colour free ions: