Modern Chemical Diagnostics

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technology

With you today

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Agenda

1. Dissolved gas analysis and its interpretation
2. Historical development of diagnostics
3. Uncertainty of dissolved gas analysis
4. Uncertainty of diagnostics
5. The importance of extraction techniques
6. Stray gassing
7. Case study 1
8. Case study 2

Dissolved gas analysis and its interpretation

The interpretation of dissolved gas analysis results requires considerable skill and several methods are available to assist.

Diagnostic methodologies

Several methods were introduced since the 1970's.

1. Statistic threshold
2. Rogers
3. Halstead
4. LCIE
5. Laborelec
6. GE
7. Church
8. Dörnenberg
9. Potthoff
10. Shanks
11. Trilinear Plot
12. IEC
13. IEEE
14. Duval

Diagnostic methodologies

1. Key gases: (Main Tank, Tap Changers): CH_4, C_2H_6, C_2H_4 and C_2H_2
2. Gas limits: CH_4, C_2H_6, C_2H_4, C_2H_2, CO and CO_2.
   a. IEC BS-EN 60599: (Main Tank, Tap Changers)
   b. IEEE C57.104, C57.130: (Main Tank)
   c. Combustible gases: (Main Tank) TDCG

Diagnostic methodologies

3. Gas Ratios,
   a. IEC BS_EN60599 Main Tank: C_2H_2/C_2H_4, CH_4/H_2, C_2H_4/C_2H_6
   b. IEEE C57-104, C57-130 Main Tank
      I. Doernenburg Ratios: CH_4/H_2, C_2H_2/C_2H_4, C_2H_2/CH_4, C_2H_6/C_2H_2
      II. Roger's Ratios: CH_4/H_2, C_2H_6/CH_4, C_2H_4/C_2H_6, C_2H_2/C_2H_4
   c. Duval's Triangles (polygon) (Main Tank)

Diagnostic methodologies

3. Gas Ratios,

   d. Duval's Triangle 1: $100*(CH_4/(CH_4+C_2H_4+C_2H_2))$ etc.

   e. Duval's Triangle 4: $100*(H_2/(H_2+CH_4+C_2H_6))$ etc.

   f. Duval's Triangle 5: $100*(CH_4/(CH_4+C_2H_4+C_2H_6))$ etc.

   g. Duval's Triangle 2 OLTC: $100*(CH_4/(CH_4+C_2H_4+C_2H_2))$ etc.

   h. MR VR OLTC: $100*(C_2H_4+C_3H_6)/(C_2H_6+C_3H_8))$, $100*(CH_4/C_2H_4)$, $100*(C_2H_2/C_2H_6)$.

Diagnostic methodologies

3. Gas Ratios,

   i. MR VV OLTC: 100*(C_2H_4 /C_2H_6), 100* (CH_4/C_2H_4), 100*(C_2H_2/ C_2H_6)

   j. MR W OLTC: 100*(C_2H_4+ C_3H_6)/(C_2H_6+C_3H_8)), 100*(CH_4/C_2H_4), 100*(C_2H_2/ C_2H_6)

   k. Doble OLTC: (C_2H_4/C_2H_2), (CH_4/C_2H_2), ((H_2+C_2H_2)/(TDCG-CO))

Diagnostic methodologies

3. Gas Ratios,
   a. Ratio Method OLTC
      I. $[(CH_4+C_2H_6+C_2H_4)/(H_2+CH_4+C_2H_6+C_2H_4+C_2H_6)]<0.5$
      II. $[(CH_4+C_2H_6+C_2H_4)/(C_2H_2)]<2.0$
      III. $[C_2H_4)/(C_2H_2)]<1.0$

4. Duval’s Triangles (polygon) (Main Tank)

Diagnostic methodologies

5. Delta X - normalised energy intensity.
6. Trend analysis.
7. Pattern recognition.
8. Fingerprinting.
9. Scoring technique.
10. Rate of gas generated

Diagnostic methodologies

But what is the common denominator
of the above mentioned techniques
with perhaps the exception of
the key gases technique?

Diagnostic methodologies

In the battle between the Intellect and the senses, the senses is always the winner!

Poor Intellect, said the senses, are you attempting to defeat us? When you are borrowing your very knowledge from us? Your victory is in fact your defeat.

Democretus 480 b.c.

Uncertainty of results - reproducibility

IEC 60567:201 Sets the result Reproducibility at 20% for medium concentrations.

ASTM D3612:2017 uses a different approach. It considers that Reproducibility is a function of concentration, according to the equation.

$I_n(R)_{95\%} = K_n(R)_{95\%} \times C_n$ Where C_n = the concentration level of gas n in ppm
$I_n(R)_{95\%}$ = the Reproducibility coefficient interval at the 95% confidence level and

Gas	CO_2,	C_2H_4,	C_2H_2,	C_2H_6,	H_2,	CH_4,	CO.
$K_n(R)_{95\%}$	0.76,	0.82,	0.64,	0.37,	0.38,	0.72,	0.79.

Ranging from 18% to 63% x concentration for different gasses.

Uncertainty in diagnostics

Considering as the best scenario of uncertainty on results, the 20% suggested by IEC we then

have; σ= 20 for a single gas such as a limit of a key gas.

The Variance σ^2_{sum} of two or more independent normally distributed random variables, is the sum of the variances; $\sigma^2_{sum} = \sigma^2_1+\sigma^2_2+\dots\dots\dots+\sigma^2_n$

The Variance σ^2_{ratio} of two or more independent normally distributed random variables, is the sum of the variances; $\sigma^2_{ratio} = (100*\sigma_1/\mu_1)^2+(100*\sigma_2/\mu_2)^2$

Thus for Duval's Triangle uncertainty at a 20% measurement uncertainty, we have for each side of the triangle;

Numerator σ_N=20, Denominator σ_D=SQRT(20^2+20^2+20^2)=34.64

And Ratio (since is already described in percentage) σ^2_T=20^2+34.64^2

or Uncertainty of σ_T=40% for each side of the triangle

Dissolved gas analysis

Gas extraction techniques

1. Total extraction
    1. Toeppler vacuum extraction
    2. Mercury-less vacuum extraction
    3. Gas stripping
2. Partial extraction
    1. Head space.
    2. Partial gas stripping.

Dissolved gas analysis

Total versus partial extraction

1. Total extraction

    1. Extracts all gases >99.9%.
    2. Utilises mild conditions.
    3. Uses vacuum & stirring.
    4. No algorithm needed.
    5. Slightly prone to air ingress.

2. Advantages & disadvantages

    1. Can be automated.
    2. No preparation step.
    3. No matrix interference.
    4. Sample volumes 5-250ml.
    5. Higher sensitivities.
    6. Earlier warning.
    7. Absolute values.
    8. Higher accuracy.
    9. Better precision.
    10. More accurate ratios of gases.
    11. Faster analysis time.
    12. Lower instrument down time.
    13. Better historical profile.
    14. But labour intensive.

Dissolved gas analysis

Total versus partial extraction

1. Partial extraction

    1. Equilibrates gases once between Liquid & Gas phase.
    2. Extracts different gases at different proportions.
    3. Extraction is concentration dependent.
    4. Utilises moderate conditions.
    5. Uses Temperature.
    6. Algorithm is necessary.
    7. Prone to air ingress
    8. Prone to matrix.

2. Advantages & disadvantages

    1. Automation.
    2. Small sample volume <16ml.
    3. Run unattended.
    4. But extraction is measurand dependant.
    5. Extracts different gases at different proportions.
    6. Exposed to matrix interference.
    7. Prone to air ingress.
    8. Requires a calculating algorithm.
    9. Uses temperature.
    10. Uses a large quantity of inert gas

Diagnostic methodologies

The Science of Analytical Chemistry
sets one extremely important rule:

One can never measure anything with any degree of confidence if the outcome depends on the measurand!

An extract from CIGRE Group WG15

It has been observed[4] that k values may vary depending on the matrix of gases present in oil. For instance, with all types of oils they are 10% lower for hydrogen when using 1% mixtures of hydrogen in air rather than pure hydrogen. With silicone oils they are 8% lower for carbon monoxide. **They also depend on the high or low levels of air, nitrogen or fault gases present in oils**, and may thus be different in sealed and air-breathing equipment. They depend on the chemical composition of oils and are different in oxidized oils[6] and in the presence in oil of chemicals such as acetone [2,4-6].

An extract from CIGRE Group WG15

A more direct and reliable method for the determination of partition coefficients has been developed by WG15[4]. It consists in bubbling in oil pure gases or 1% mixtures of these gases in air up to equilibrium, extracting these gases completely using Toepler or Partial Degassing with multiple cycles of vacuum extraction, then measuring the total volume of gas extracted.

Stray gassing - definition

The phenomenon of generation of gases, at moderate temperatures (a hot spot temperature less than 120ºC) and in the absence of any fault (thermal or electrical), in a transformer oil is known as stray gassing.

Initially, hydrogen was observed and considered as the only gas contributing to stray gassing. More recently carbon monoxide, methane, ethane and even ethylene has also been observed.

Stray gassing - outcome

Dissolved gas analysis results does not necessarily distinguish between a stray gassing condition and a fault condition.

Stray gassing known facts so far

I. Stray gassing generates –amongst heavier molecules- the same small gas molecules involved in diagnostics. Namely; H_2, CH_4, C_2H_6, C_2H_4, but also C_3H_8, and C_3H_6.

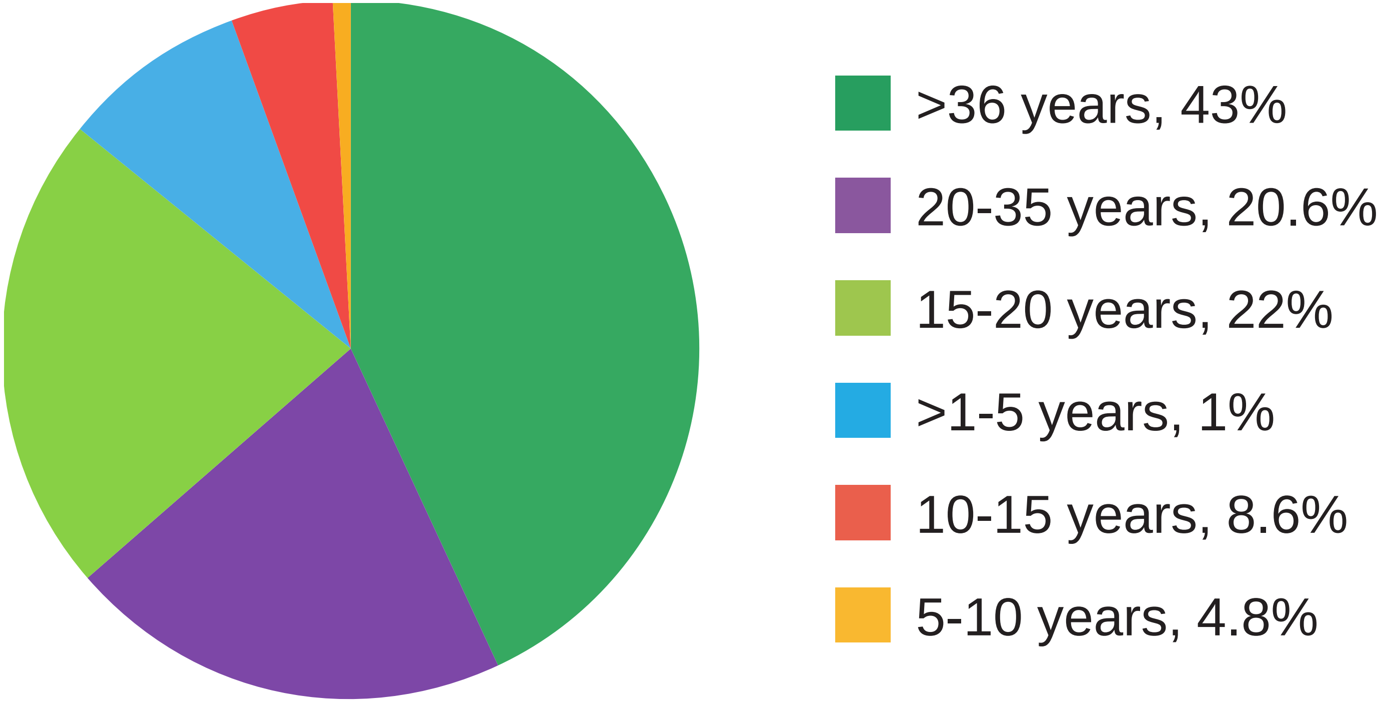
II. The gases are produced under moderate temperatures and in the absence of electrical activity.

III. The production is continuous, but at varying rates governed by reaction kinetics.

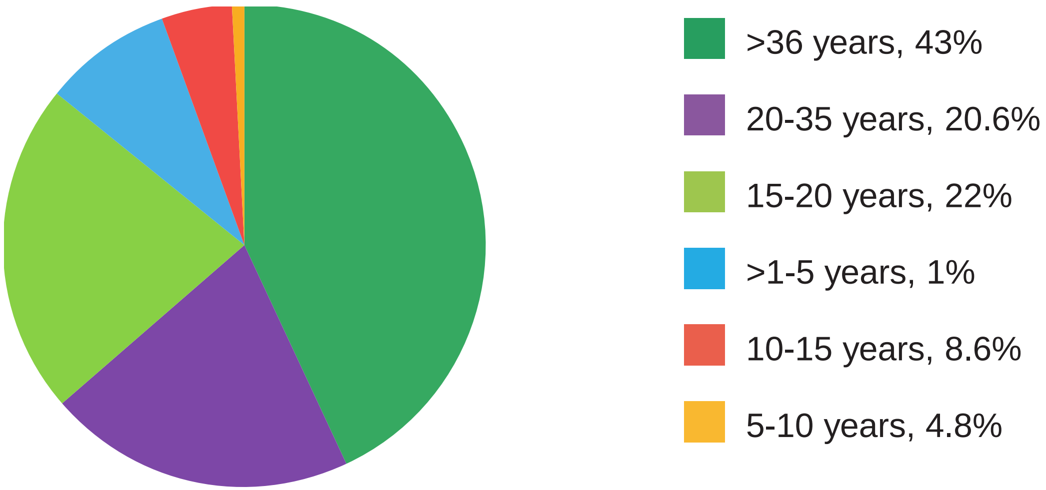
IV. The gas generation is accelerated or catalyzed by various promoters known as “sensitisers”.

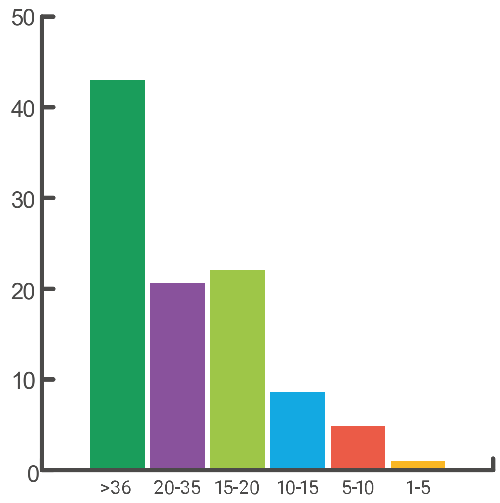
V. Their presence disrupts the normal diagnostic assessment process.

Percentage of transformers stray gassing versus age



Percentage of transformers stray gassing versus age





% Tx	No. of Tx	Approx. years
43	125	>36 years
20.6	60	20-35 years
22	64	15-20 years
8.6	25	10-15 years
4.8	14	5-10 years
1.0	3	1-5 years

The gases generated

Gases	Hydrogen (H_2)	Methane (CH_4)	Ethane (C_2H_6)	Ethylene (C_2H_4)	Propane (C_3H_8)	Propelene (C_3H_6)
Observation	Moderate to high values	Moderate to high values	Moderate to high values	Relatively low values	Moderate to high values	Moderate to high values
Appears in Tx of	All ages	All ages	All ages	All ages	All ages	All ages
Profile	Increases during the first years	Increases during the first years	Increases during the first years	A small increase	Increases during the first years	Increases during the first years
Natural Esters Show		Higher values	Higher values		Higher values	Higher values
Synthetic Esters		Intermedia values	Intermedia values		Intermedia values	Intermedia values
Rate of increase	1 - 9 ppm/day	1 - 7 ppm/day	1 - 5 ppm/day	0 -1.5 ppm/day	1 - 5 ppm/day	1 - 3 ppm/day
Dependency	Temperature, Load	Degree of Curing	Presence of Sensitisers	Incompatibility Products	Oil Stability	Presence of Oxygen

The gases generated – used oils

Gases	Hydrogen (H_2)	Methane (CH_4)	Ethane (C_2H_6)	Ethylene (C_2H_4)	Propane (C_3H_8)	Propelene (C_3H_6)
Observation	Moderate to high values	Moderate to high values	Moderate to high values	Relatively low values	Moderate to high values	Moderate to high values
Appears in Tx of	All ages	All ages	All ages	All ages	All ages	All ages
Profile	Increases during the first years	Increases during the first years	Increases during the first years	A small increase	Increases during the first years	Increases during the first years
Natural Esters Show		Higher values	Higher values		Higher values	Higher values
Synthetic Esters		Intermedia values	Intermedia values		Intermedia values	Intermedia values
Rate of increase	1 - 25 ppm/day	1 - 10 ppm/day	1 - 7 ppm/day	0 - 5 ppm/day	1 - 8 ppm/day	1 - 4 ppm/day
Dependency	Temperature, Load	Temperature, Load	Temperature, Load		Temperature, Load	Temperature, Load

The gases generated

Test	Method	Units	New	Used
Stray Gassing Air Purge	ASTM D7150		Oil	Oil
Hydrogen	IEC60567	mg/kg*day ppm/day	1-9	1-25
Methane	IEC60567	mg/kg*day ppm/day	1-7	1-10
Ethane	IEC60567	mg/kg*day ppm/day	1-5	1-7
Ethylene	IEC60567	mg/kg*day ppm/day	1-1.5	1-5
Propane	IEC60567	mg/kg*day ppm/day	1-5	1-8
Propylene	IEC60567	mg/kg*day ppm/day	1-3	1-4

The gases generated

1. Gas ratios observed; C_2H_6/C_2H_4 >10 and C_3H_8/C_3H_6 >10
2. The above ratios may be larger for older transformers.
3. Consumption of oxygen is also observed and the ratio of O_2/N_2 <0.35
4. This also explains the presence of carbon monoxide as a stray gas.

What causes stray gassing?

1. It is thought that one of the causes is severe hydrotreating of the oil during refinery production.
2. Transformer material such as the grain oriented steel, or zinc plated steel.
3. Paints and varnishes, glues and epoxy bonding materials particularly if no sufficient amount of curing time has not been given.
4. Any type of incompatibility of construction materials may be a source of gassing.
5. Any contaminant in the oil that can act as a sensitiser.

Ways to deal with stray gassing

1. Observe rate of increase in in two or more consecutive tests)CO, H_2, CH, C_2H_6 and C_3H_8, and C_3H_6 also observe ratio of O_2/N_2 if <0.4.
2. Examine and compare the rate of increase in concentration of the above mentioned gases.
   I. If there is a regular pattern of increase (similar increase in all gases in two or more consecutive tests) then there is a strong suggestion for stray gassing. Perform stray gassing analysis to confirm.
   II. If the rate of increase is different or higher than 5 ppm/day then there might be a fault developing. Stray gassing information might still be needed to establish type and severity of fault.

Summary

- Dissolved gas analysis has developed through out the years, but it has not always moved forward.
- As a result both research and diagnostics has experienced the consequences.
- Total extraction is by far the most accurate technique for oil analysis, but we have already moved away from it.
- Stray gassing is another threat masking diagnostics.

Summary of benefits

Better understanding of processes

Extend asset life

Maintain leadership within the industry

Generate opportunities

Research collaboration
An example case study

Stray gassing – a case study 1

Dissolved gas analysis results

Date	CO_2	C_2H_4	C_2H_2	C_2H_6	H_2	CH_4	CO	TDCG	FAULT
12/04/19	584.3	1291.5	0.1	169.2	141.0	484.9	54.2	2140.9	T_3
14/01/19	681.9	1274.8	0.0	177.6	175.5	450.5	73.5	2151.9	T_3

Stray gassing – a case study 1

Stray gas analysis results

Purge	CO_2	C_2H_4	C_2H_2	C_2H_6	H_2	CH_4	CO	TDCG
N_2	34.2	4.45	0.00	35.72	88.12	28.62	132.07	288.98
N_2	35.1	4.49	0.00	35.54	87.83	28.46	131.18	287.50
AV	34.65	4.47	0.00	35.63	87.98	28.54	131.63	288.24

Stray gassing – a case study 1

Stray gas analysis results

Purge	CO_2	C_2H_4	C_2H_2	C_2H_6	H_2	CH_4	CO	TDCG
Air	498.56	9.51	0.00	44.82	342.02	37.78	753.20	1187.33
Air	486.93	9.97	0.00	45.46	337.30	37.74	751.80	1218.27
AV	492.72	9.74	0.00	45.14	357.66	37.76	752.50	1202.80

Stray gassing – a case study 1

Rate of change versus stray gas results

Rate as ppm/day	C_2H_4	C_2H_2	C_2H_6	H_2	CH_4	CO	TDCG
N_2	0.65	0.00	5.21	12.88	4.18	19.26	42.18
Air	1.43	0.00	6.61	52.34	5.53	110.12	176.02
Rate of change	0.19	0.001	-0.10	-0.40	0.40	-0.22	-0.13

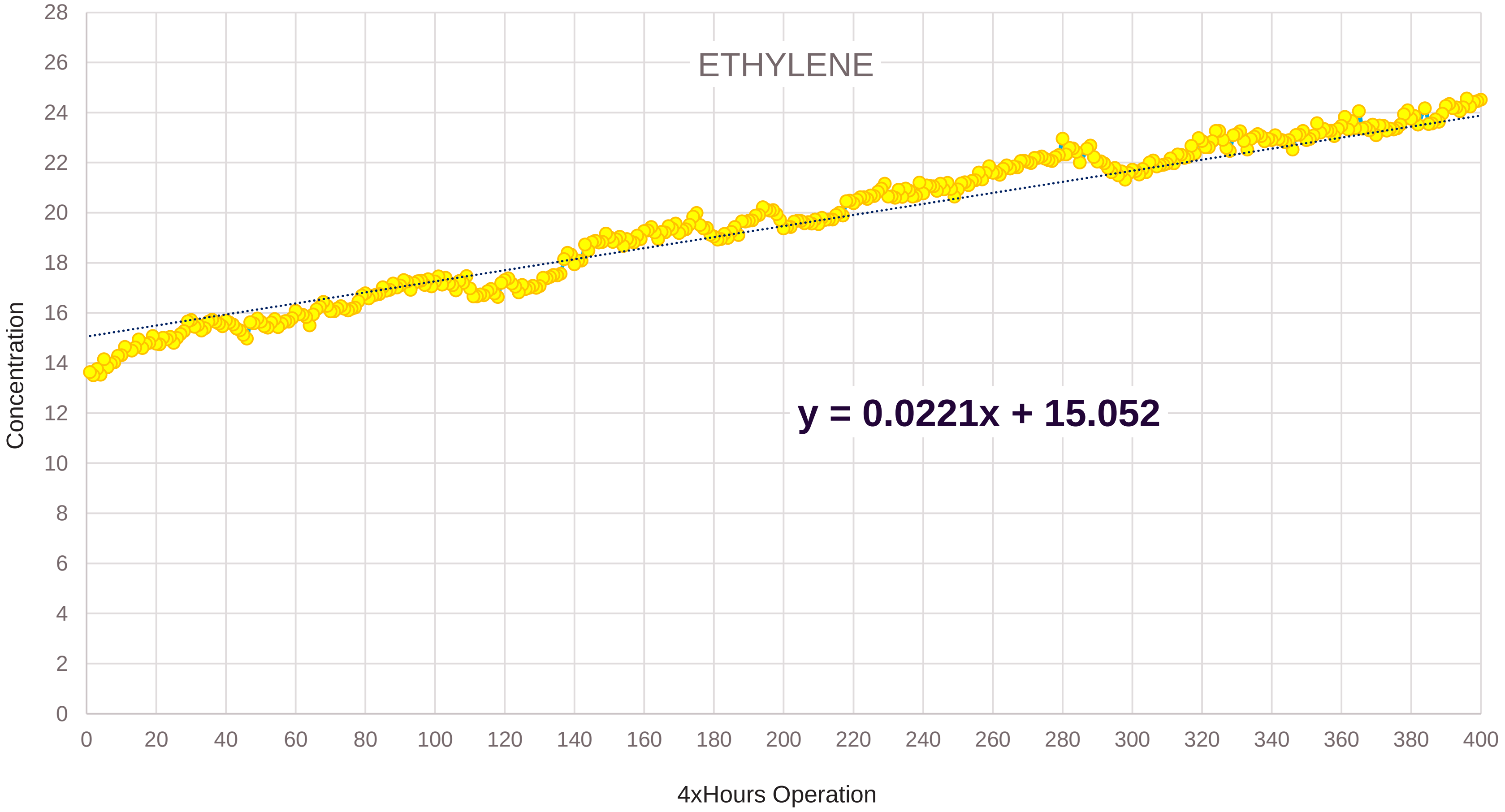
Stray gassing – a case study 2

An example – ABB 48/48/16 MVA 132kV/36kV

C2H2			C2H4			C2H6			CO	
Conc	Conc change	Evolution rate	Conc	Conc change	Evolution rate	Conc	Conc change	Evolution rate	Conc	Conc change
ppm	ppm	ppm/4xhou	ppm	ppm	ppm/4xhou	ppm	ppm	ppm/4xhou	ppm	ppm
0.51	-0.05	-0.0113	25.92	-0.33	-0.0815	3.58	-0.30	-0.0757	282.85	0.63
0.56	0.04	0.0100	26.25	0.07	0.0175	3.88	-0.66	-0.1648	282.22	-0.95
0.52	0.10	0.0238	26.18	-0.17	-0.0415	4.54	0.43	0.1087	283.17	-0.52
0.42	-0.22	-0.0542	26.35	0.08	0.0194	4.11	-0.29	-0.0737	283.70	0.03
0.64	0.07	0.0177	26.27	0.34	0.0847	4.40	0.38	0.0960	283.67	-0.52
0.57	0.14	0.0361	25.93	-0.22	-0.0556	4.02	0.49	0.1223	284.19	1.17
0.42	-0.16	-0.0389	26.15	-0.28	-0.0688	3.53	0.07	0.0167	283.02	0.20
0.58	-0.07	-0.0165	26.43	0.24	0.0597	3.46	-0.46	-0.1154	282.82	-0.60
0.65	0.04	0.0098	26.19	-0.18	-0.0448	3.92	0.07	0.0167	283.42	-1.41
0.61	0.28	0.0692	26.37	-0.16	-0.0400	3.86	-1.31	-0.3268	284.83	0.09
0.33	-0.05	-0.0134	26.53	0.28	0.0704	5.16	0.94	0.2341	284.74	-0.56
0.38	-0.07	-0.0175	26.25	0.09	0.0235	4.23	0.19	0.0473	285.30	1.42
0.45	0.04	0.0106	26.15	-0.26	-0.0660	4.04	-0.36	-0.0892	283.89	0.23
0.41	-0.09	-0.0217	26.42	-0.13	-0.0325	4.39	0.24	0.0601	283.65	0.09

Stray gassing – a case study 2

An example – ABB 48/48/16 MVA 132kV/36kV - **first derivative**



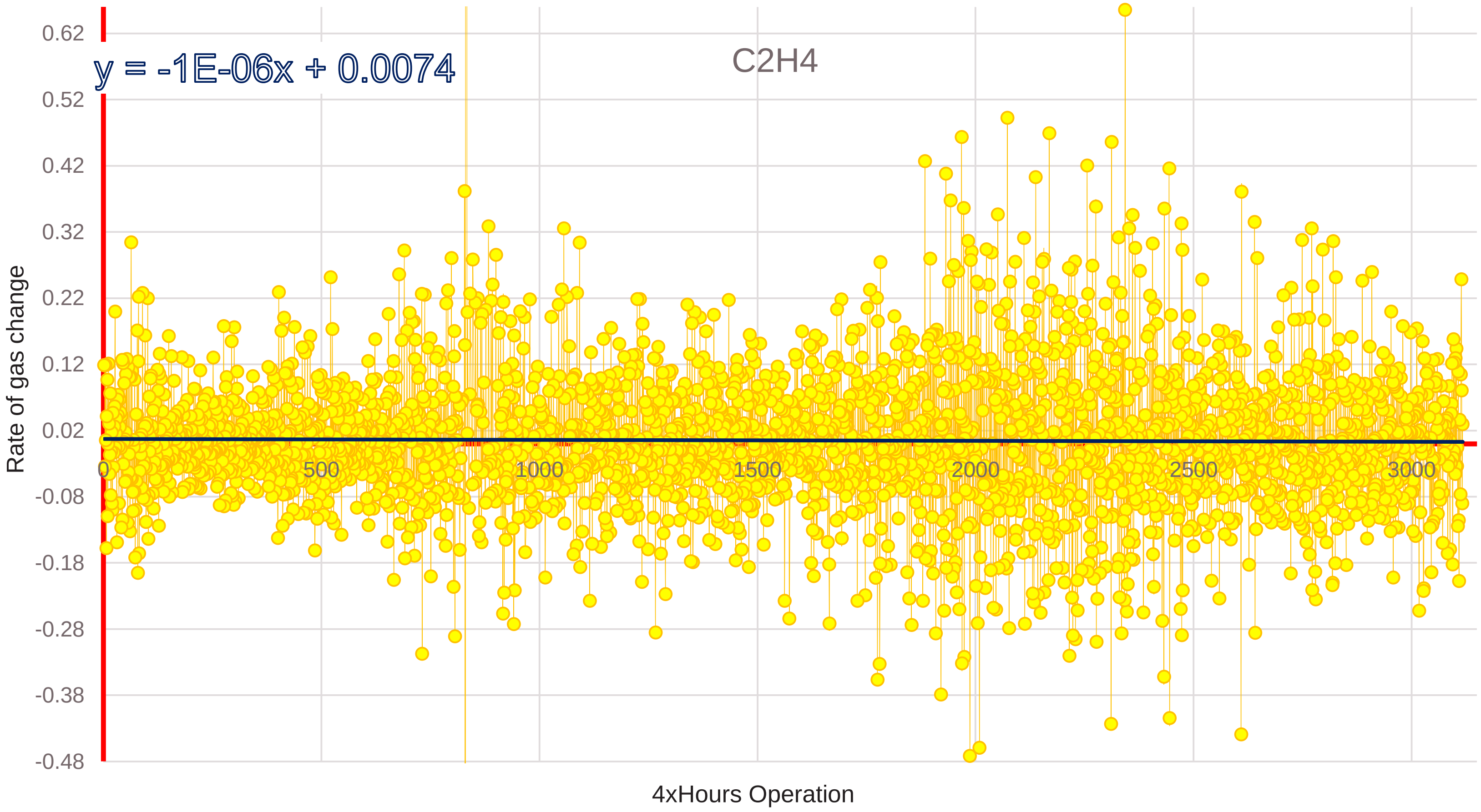
Stray gassing – a case study 2

An example – ABB 48/48/16 MVA 132kV/36kV

Rate (ppm)	H2	CH4	C2H2	C2H4	C2H6	CO	TDCG	O_2/N_2	CO_2/CO	
4xHour	0.0032	0.0021	0.0002	0.0172	0.0017	0.1824	0.2068	-0.00001	-0.0019	ConCGraph2
Day	0.0192	0.0126	0.0012	0.1032	0.0102	1.0944	1.2408	-0.00006	-0.0114	
2nd Derivative	Neg	Neg	Neg	Neg	Neg	Neg		Neg	Pos	
4xHour	0.00100	0.00270	0.00008	0.02210	-0.00530	0.20160	0.2222	-0.00005	-0.00420	ConCGraph1
Day	0.0060	0.0162	0.0005	0.1326	-0.0318	1.2096	1.3331	-0.0003	-0.0252	
2nd Derivative	Pos	Pos	Pos	Pos	Neg	Neg		Neg	Pos	

Stray gassing – a case study 2

An example – ABB 48/48/16 MVA 132kV/36kV - **second derivative**



Stray gassing – a case study 2

An example – ABB 48/48/16 MVA 132kV/36kV

Dissolved gas analysis following thermal stress

N2 Purged						
Sample	H2	CH4	C2H6	C2H4	C2H2	CO
A	6.883	49.905	11.546	20.365	0.000	497.215
B	6.837	48.735	10.993	20.972	0.000	479.983
Average	6.860	49.320	11.270	20.669	0.000	488.599
Air Purged						
Sample	H2	CH4	C2H6	C2H4	C2H2	CO
A	17.535	28.493	7.741	26.996	0.000	684.333
B	16.994	28.078	6.897	25.784	0.000	679.875
Average	17.2645	28.286	7.319	26.390	0.000	682.104

Stray gassing – a case study 2

An example – ABB 48/48/16 MVA 132kV/36kV

Stray gas rate production

Gas N2 Purged	H2	CH4	C2H6	C2H4	C2H2	CO
ppm/164hours	6.860	49.318	11.269	20.661	0.000	488.596
Rate ppm/day	1.00	7.22	1.65	3.02	0.00	71.50
ppm/164hAir Purged	17.265	28.281	7.318	26.381	0.000	682.094
Rate ppm/day	2.53	4.14	1.07	3.86	0.00	99.82

Stray gassing – a case study 2

An example – ABB 48/48/16 MVA 132kV/36kV

Stray gas analysis

Gases as ppm/day	H_2	CH_4	C_2H_6	C_2H_4	C_2H_2	CO
Transfix1	0.019	0.013	0.010	0.103	0.001	1.094
Transfix2	0.006	0.016	<0	0.133	0.001	1.210
Headspace1	0.000	0.001	0.006	0.073	<0	0.109
Headspace2	0.017	0.006	<0	0.121	<0	1.617
Stray Gassing Air Purge	2.527	4.139	1.071	3.861	0.000	99.819

Thank you

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