SAIOH 2013

Interpretation of Elemental Analyses Results

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WHY AEROSOL SAMPLING?

- Air sampling for aerosols, to determine the airborne concentrations of particulate matter, forms a major component of the duties of many Occupational Hygiene Professionals.
- Considering all the types of aerosols sampled and submitted for subsequent laboratory analyses, one realizes that dusts and fumes of inorganic composition represent a major component of the total number of airborne aerosols sampled for Occupational Hygiene purposes.

WHAT IS DUST?

- We (some of us) realize that the term “dust” does not refer to a substance with a universal Safe or Sub-hazardous Exposure Limit (or Occupational Exposure Limit).

(“Dust” refers more to the state of matter than it refers to its composition)

- So when we measure dust exposure, we are faced with the dilemma of how to evaluate and conclude whether a given dust concentration (or exposure level) is considered “safe” or sub-hazardous, or not.

WHY ANALYZE?

- Understanding that the composition of dust, somehow, has relevance to its hazard potential, which thus forms the basis from which a Safe or Sub-hazardous Exposure Limit can be derived, such inorganic dusts are commonly submitted for analyses to determine the dust's elemental content.
- Many OH Professionals then indiscriminately compute the airborne concentrations for each of the elements reflected in the dust sample's analysis report and compare these concentrations to the nearest resembling or best fitting OEL.
- From this "scientific evidence", conclusions are then made regarding the exposed individual's or group's risks, regarding exposure to the original dust.

All very simple, except that it is too simple and completely incorrect in most cases

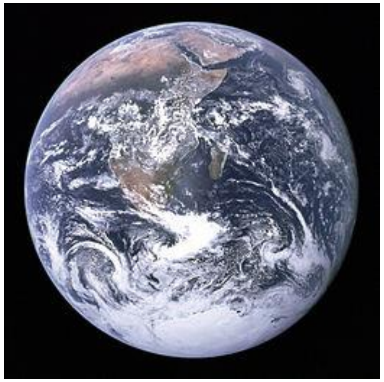
WHAT IS DUST (TALKING ABOUT NATURAL OCCURRING DUST THAT IS AROUND US ALL THE TIME)?

- When you inhale dust, what are you actually exposed to?
- Why do we analyze dust samples?
- After receiving the analyses results, which OELs do one apply?

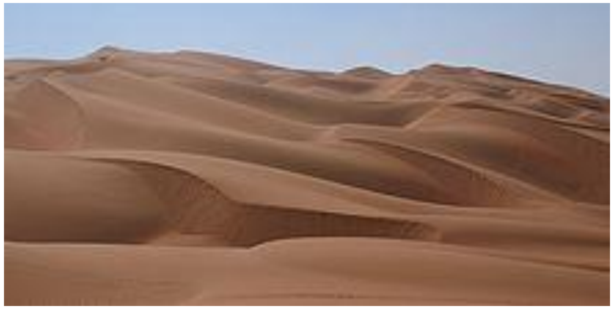
To answer these questions, one must first understand what (natural occurring) "dust" is.

WHAT IS DUST?

- This is the earth – **we only know what is going on, on its surface (the solid Crust/Lithosphere; 0 – 35km deep).**



There are also some mountains/rocks and deserts/sand



WHAT IS DUST?

- On the Earth's surface, we get rocks **(mountains are big "rocks" and rocks are fragments of mountains).**
- A **dust** particle, is merely a very small fragment of a **rock.**
- A **rock/dust particle**, comprise of **minerals** - usually more than one (the term mineral is synonymous with the terms compound and molecule).
- And a **molecule** is made up of **elements** (atoms) that are bonded together

DUST – AN EXAMPLE

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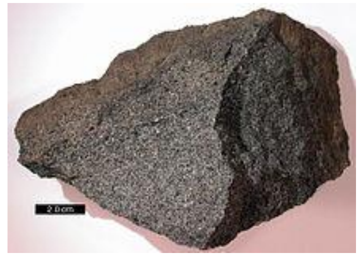
Granite (Rock) - Dust



Quartz
(SiO_2)

Minerals
(molecules or compounds)

Amphibole
$((Mg/Ca,Fe)_7Si_8O_{22}(OH)_2)$

Feldspar
$(KAlSi_3O_8)$

Muscovite
$(KAl_2(AlSi_3O_{10})(F,OH)_2)$

Si/O

Ca, or Mg, Fe, Si/O, H

K, Al, Si/O

Elements
metal/non-metal

K, Al, Si/F, O, H

ICP ANALYSES

- So how do the laboratories go about analyzing samples to determine the element content and respective element masses of a sample?
- The most popular method is the analysis for elements by Inductively Coupled Argon Plasma - Atomic Emission Spectroscopy (ICP-AES).
- e.g. NIOSH Method No's. 7300/1/2/3

ICP ANALYSES

- This method involves "cooking" the sample in a mixture of inorganic acids, such as Nitric-, Perchloric-, and/or Hydrochloric acid, to break the molecules (minerals or compounds) down to a solution of elements/ions (anions and cations – charged atoms);
- The granite dust sample is dissolved to a solution of Ca^{2+}, Mg^{2+}, Fe^{2+}, Si^{4+}, K^{+}, Al^{2+}, F^{-}, H^{+} and OH^{-}.

The acid completely destroyed the original structures of the minerals, leaving you with a soup of dissolved elements

ICP Analyses

- From the above, the Laboratory will provide you with results as follows, for example:

Element	Result	Element	Result
Aluminium, Al	0.110	Potassium, K	0.055
Calcium, Ca	0.267	Magnesium, Mg	0.111
Iron, Fe	0.702	Silicon, Si	0.235

Note:

Results in milligram per sample (mg/sample)

RESULT INTERPRETATION – IRON AS EXAMPLE

The Iron (Fe) Result:

- Would it be correct to take the Iron (Fe) value of 0.702 mg, divide it by the sample volume to get a mg/m^3 concentration and compare that value with the OEL for Iron Oxide fumes (Fe_2O_3 – as Fe) of 5 mg/m^3?
- Yes/No?

RESULT INTERPRETATION – IRON AS EXAMPLE

The Iron (Fe) Result:

- Most definitely No!

We sampled dust not fume, and the source molecule is Amphibole ($(Mg/Ca,Fe)_7Si_8O_{22}(OH)_2$), not Fe_2O_3 - they are just not the same thing!

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Why/why not using any of the following OHS Act OELs for Iron – perhaps the OEL for Iron salts?:

Substance	Occupational Exposure Limit			
	TWA OEL-RL ppm	TWA OEL-RL mg/m³	Short Term OEL-RL ppm	Short Term OEL-RL mg/m³
Iron Oxide, fumes – as Fe (Fe_2O_3)	-	5	-	10
Iron pentacarbonyl - as Fe ($Fe(CO)_5$)	0.01	0.08	-	-
Iron salts soluble - as Fe	-	1	-	2
Rouge: Total Inhalable dust Respirable dust		 10 5		

RESULT INTERPRETATION – CALCIUM AS EXAMPLE

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The Calcium (Ca) Result:

- Would it be correct to take the Calcium (Ca) value of 0.267 mg, divide it by the sample volume to get a mg/m^3 concentration and compare that value with the OEL for Calcium Oxide, (CaO) of 2 mg/m^3?
- Yes/No?
- Why/why not?

RESULT INTERPRETATION – CALCIUM AS EXAMPLE

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The Calcium (Ca) Result:

- Firstly, you cannot compare the concentration of “Ca” with the OEL of “CaO” – you just can’t because they are not the same substances – ***you will have to calculate the CaO mass equivalent of your Ca result first, then calculate the CaO concentration, then compare with the CaO OEL***

But, that would still be the wrong thing to do in this case!

RESULT INTERPRETATION – CALCIUM AS EXAMPLE

The Calcium (Ca) Result:

- Secondly, the source of Ca in your results was Amphibole ($(Mg/Ca,Fe)_7Si_8O_{22}(OH)_2$), and not CaO

RESULT INTERPRETATION – CALCIUM AS EXAMPLE

Could we apply any of the following Calcium OELs

Listed in the OHS Act for our Ca result?:

See Next Slide

RESULT INTERPRETATION – CALCIUM AS EXAMPLE

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Substance	Occupational Exposure Limit			
	TWA OEL-RL ppm	TWA OEL-RL mg/m³	Short Term OEL-RL ppm	Short Term OEL-RL mg/m³
Calcium carbonate ($CaCO_3$):				
Total Inhalable dust	-	10	-	-
Respirable dust	-	5	-	-
Calcium cyanamide (CaNC≡N)		0.5		1
Calcium hydroxide ($Ca(OH)_2$)		5		
Calcium oxide (CaO)		2		
Calcium silicate:				
Total Inhalable dust	-	10	-	-
Respirable dust	-	5	-	-
Gypsum ($CaSO_4.2H_2O$):				
Total Inhalable dust	-	10	-	-
Respirable dust	-	5	-	-
Limestone:				
Total Inhalable dust	-	10	-	-
Respirable dust	-	5	-	-
Marble:				
Total Inhalable dust	-	10	-	-
Respirable dust	-	5	-	-
Plaster of Paris [$(CaSO_4)_2.H_2O$]:				
Total Inhalable dust	-	10	-	-
Respirable dust	-	5	-	-

RESULT INTERPRETATION – CALCIUM AS EXAMPLE

- **So many choices – which one do you choose?:**
  - Of all the OELs to choose from, the OEL for Calcium silicate seems to be a reasonable match, since one of the minerals in the Granite dust sample is a Silicate mineral; **Amphibole** $(Ca,Fe)_7Si_8O_{22}(OH)_2)$ – a Calcium-Iron Silicate, hydroxide.
  - However, Calcium silicate has the formula of $CaSiO_3$, which occurs naturally as the mineral Wollastonite (the OEL for $CaSiO_3$ is specific to this substance – nothing else).

A clear mismatch, in which case not even the Calcium silicate OEL is applicable to the Ca result received from the laboratory.

Rule Number 1:

- One cannot assume that exposure to a particular element occurred, just because that element is reflected in an analysis report ***(the element is probably, merely an atom that is part of a larger, more complex molecule – the trick is to figure out which one).***

THE MORAL OF THE STORY

- **Considering the example of the Iron and Calcium results:**
  - The subject was not exposed to either Iron or Calcium. He/she was exposed to a mineral/molecule that happened to have Iron and Calcium in its makeup.
  - The molecule (Amphibole) to which the subject was actually exposed does not have the same chemical, physical or toxicological properties as either Iron, or Calcium – ***more reason why OELs for random Calcium-, or Iron compounds cannot be valid.***

Rule Number 2:

- One may only apply an OEL if exposure to the substance for which the OEL is intended occurred (a 100% match, not merely a resemblance).

i.e. you may only apply the OEL for Iron oxide fume - (Fe_2O_3), if it is 100% certain that exposure to Iron oxide fume - (Fe_2O_3) occurred; not Iron oxide dust, (such as Hematite and Rouge which are mineral forms of Fe_2O_3) nor Iron oxide in the form of Fe_3O_4 (e.g. rust and mill-scale or Magnetite) either!

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Rule Number 2 (major confusion in legislation):

- **Under the MHSA OELs, Fe_2O_3 (Iron oxide) dust OEL = 5mg/m^3 TIP, but,**
- **Rouge OEL = 10mg/m^3 TIP, but,**
- **Fe_2O_3 (Iron oxide) and Rouge is one and the same thing (even have the same CAS numbers) – explain that?**

Unfortunately our current legislation has too many such discrepancies

Rule Number 3:

- It is not up to the laboratory to tell one what the subject was exposed to – ***the one that submits the sample for analyses must have a specific reason and expectation***
- The Laboratory performs analyses according to strict protocol, and issues standardised results – **it is the OH professional's responsibility to know how to interpret the result (which OEL to apply).**

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***This is why it is crucial that OH professionals need to have a good understanding of chemistry in general, but also pertochemistry, process chemistry and analytical chemistry*.**

Our profession involves much more than the knowledge of sampling techniques, and the health hazards of a few selected substances.

THE SHORT STORY OF CALCIUM

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The most common natural form of calcium Ca_2CO_3 (Calcium carbonate) a.k.a:

- Aroganite (mineral)
- Calcite (mineral)
- Limestone, Marble (rocks, comprising of Calcium carbonate)
- Egg shell
- Mollusk shell
- Vertebrate animal skeletons
- Coral
  - OEL of 10mg/m^3 Total Inhalable dust and 5mg/m^3 for Respirable dust

THE SHORT STORY OF CALCIUM

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Ca_2CO_3 —Heat (Kiln/Calcining)→ $CaO + CO_2$

Ad (H_2O) Water/vapor ↓

$Ca(OH)_2$

CaO:

- Calcium oxide
- Un-slaked Lime
- Dehydrated Lime
- Calcium fume (from smelting, welding, etc.)
  - Highly alkaline and highly reactive
  - OEL = 2mg/m^3 TIP

$Ca(OH)_2$:

- Calcium hyoxide
- Slaked Lime
- Hydrated Lime
  - Highly alkaline <u>but not </u>highly reactive
  - OEL = 5mg/m^3 TIP

The Short Story of Calcium

What happens to a Calcium compound in welding or smelting process:

- **The heat convers the compound (molecule) to its elemental state to produce free airborne Calcium (Ca) atoms**
- **Ca atoms are highly reactive and immediately react wit atmospheric Oxygen (O_2) to produce CaO (Calcium-oxide) fume**
- **CaO itself is highly reactive and will immediately react with atmospheric water (H_2O), to produce Calcium hydroxide ($Ca(OH)_2$) – and that is what a welder or Furnace operator is exposed to – $Ca(OH)_2$ with an OEL of 5mg/m^3 TIP**

But – the Lab only gives you a result for "Ca"!!

THE SHORT STORY WITH CALCIUM

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You (following the preceding rules) cannot compare the Calcium concentration directly with the $Ca(OH)_2$ OEL of 5mg/m^3 TIP. You will first have to calculate the equivalent mass of $Ca(OH)_2$ from the Ca mass result received from the Lab:

- **Equivalent $Ca(OH)_2$ mass =** $$\frac{\text{Lab "Ca" result}}{\text{"Ca" Atomic mass}} \times \frac{Ca(OH)_2 \text{ Molecular mass}}{1}$$

So, for example, if the Lab sent you a result for Ca of 10mg, the equivalent $Ca(OH)_2$ mass is calculated as follows:

- $$= \frac{10\text{mg}}{40} \times \frac{74}{1} = \underline{18.5\text{mg}}$$

The short story with Calcium

- **Now this 18.5mg $Ca(OH)_2$ mass can be converted to concentration (by dividing by the sample volume in m^3) and that concentration may be compared with the $Ca(OH)_2$ OEL of 5mg/m^3 TIP**

Discussion and Questions

THANK YOU

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