COD –
What is Chemical Oxygen Demand?

Dr Jeffry Guthrie-Strachan, Stephen Trantum,
and Ulrich Buckenmayer – Trumpler

Edited by: Matthew Abbott, Design by: Tim Button – World Leather

TRUMPLER SIMPLY GOOD CHEMISTRY   WORLD LEATHER

Part One: COD – What is Chemical Oxygen Demand?

Dr Jeffry Guthrie-Strachan, Stephen Trantum, and Ulrich Buckenmayer – Trumpler

We have all heard of COD but how many of us really know what it is, or what it means?

Trumpler has undertaken a five-year long investigation into the role that COD plays in its products, how COD can be used to express the exhaustion of the products, and whether or not the effluent COD of a dyehouse recipe can be predicted using data accumulated from the project. The results of the study will be outlined in Part 2 of this report in a following issue of World Leather but first we need to understand what COD represents, its importance and how and why it is measured.

To start, COD is an acronym for Chemical Oxygen Demand. The COD and solids content of sewage and trade effluents are two of the most important parameters used to calculate effluent treatment costs for tanneries.

When looking at industrial and tannery effluents, there are a number of parameters that are commonly measured, e.g., chromium, chloride, sulfide, sulfate, TKN (total Kjeldahl nitrogen), total dissolved solids (TDS), biochemical oxygen demand (BOD), and chemical oxygen demand (COD). Some of the analyses are a direct measurement of the pollutant under investigation, e.g., chromium, chloride, sulfide, and sulfate; others represent a collection of many pollutants and are not specific, such as TKN, TDS, BOD and COD. *[Table1]*

Chemical oxygen demand or COD is a relatively convenient, reproducible, and affordable way to represent the organic pollutant load of an effluent.

What are organic pollutants?

Organic compounds are chemicals composed of carbon[2] *[Box 1]*. There are millions of different chemical compounds that contain carbon and this is why organic chemistry is so important in its own right. Any organic compound that contaminates a water or soil sample is an organic pollutant.

Why is it important to measure organic pollutants (COD) in effluents?

When organic pollutants are toxic, they will kill fish and aquatic plant life and microorganisms, thereby directly damaging ecosystems and the environment. Organic tannery pollutants are generally non-toxic and are, conversely, a rich

Table 1: Common effluent pollutants and analyses[1]

Effluent Analysis	Specific or General	What does the analysis represent?	Why is it measured?
Chromium(III) and chromium(VI)	Specific	The amount of chromium present as Cr(III) and/or Cr(VI)	May form chromium(VI)
Chloride	Specific	The amount of salt (sodium chloride) present in an effluent	Increased salinity results in unpotable water and cannot be used for crop irrigation
Sulfide	Specific	The amount of sodium sulfide in an effluent	Forms toxic hydrogen sulfide gas upon acidification
Sulfate	Specific	The amount of sodium sulfate in an effluent	May form toxic hydrogen sulfide gas under anaerobic conditions
TKN	Specific/General	Represents nitrogen-based pollutants like ammonia, ammonium ions and/or organic nitrogen in an effluent	May cause eutrophication of natural waters
TDS	General	Represents the amount of dissolved organic and inorganic solids in an effluent	May cause the blockage of effluent pipes and drains
BOD	General	A representation of the biodegradable organic and nitrogen components of an effluent (usually in 5 days - BOD_5)	May cause microbial activity to increase in natural waters and create an oxygen starved aqueous environment with associated environmental damage
COD	General	A representation of the organic component of an effluent	May create an oxygen starved aqueous environment with associated environmental damage

Figure 1

Organic compounds → Decomposition of organic compounds → Microorganism growth → Aerobic respiration → Oxygen use → Oxygen depletion → Damage to aquatic animal and plant life

source of food for aquatic microorganisms. Herein lies an additional, indirect problem.

When aquatic microorganisms "eat" organic compounds, they use oxygen dissolved in the water in a process called aerobic respiration. If there is a significant amount of organic food (pollutants) present in the water, the microorganisms require a significant amount of dissolved oxygen to "digest" the food. Natural waters contain very small amounts of dissolved oxygen, only about 10 milligrams per litre of water[3], and this natural source of dissolved oxygen is easily and rapidly exhausted. Organic pollutants can thereby, indirectly, cause oxygen starvation in natural waters, which has an obvious negative impact on fish and other aquatic fauna and flora, as represented in *Figure 1*.

Where did the COD method of measuring organic pollutants come from?

When organic substances degrade and are consumed by microorganisms, oxygen is utilised in the process and the organic compounds are described as possessing an oxygen demand. This oxygen demand can be summarised using a chemical reaction for the decomposition of a simple organic hydrocarbon compound into carbon dioxide and water:

$$C_xH_y + (x+\tfrac{y}{4})O_2 \rightarrow xCO_2 + \tfrac{y}{2}H_2O$$

Organic compound + oxygen → carbon dioxide + water

This equation shows that if we can measure the amount of oxygen consumed when organic compounds decompose, we can use this value to represent how much organic compound was present at the beginning. Oxygen demand is usually expressed as milligrams of oxygen consumed (required) per litre of effluent (mg O_2/L).

BOD_5 is also an oxygen demand known as biochemical oxygen demand. BOD_5 measures the amount of oxygen consumed by microorganisms as they degrade an effluent sample over 5 days. The oxygen content of the original effluent sample is measured at the start of the analysis and then the remaining oxygen content is measured after 5 days. The difference represents the oxygen consumed biochemically by microorganisms over the period and is expressed in terms of milligrams of oxygen consumed per litre of effluent[3].

BOD_5 takes 5 days to complete, is not always consistent and can be unreliable. For this reason, chemists wanted to find a process that was faster, more reliable, consistent and affordable. They looked to chemicals that are known to react by providing a chemical source of oxygen, e.g., potassium permanganate and potassium dichromate. This approach was referred to as a chemical oxygen demand.

Potassium permanganate was used in early chemical oxygen demand methods and was referred to as "oxygen absorbed" (OA), "oxygen consumed" or "permanganate value" (PV)[3]. The results are not consistent and the method is seldom used today.

The standard chemical oxygen demand method used today utilises potassium dichromate as the chemical source of oxygen and fulfils almost all the requirements for expressing organic pollutant contents of effluents.

> **Box 1 Organic Compounds**[2]
>
> Organic compounds are substances composed of carbon, excluding (i) the elemental forms of carbon, such as graphite and diamond, (ii) the oxides of carbon, such as carbon monoxide and carbon dioxide, (iii) carbonates such as sodium carbonate, and (iv) cyanides such as sodium cyanide.
>
> Examples of COD-active organic compounds include natural fats and oils, proteins such as collagen, keratin and proteoglycans, carbohydrates (sugars), syntans, vegetable tannins, mineral oils, polymers, organic acids such as formic and lactic acid, glutaraldehyde and dyestuffs.

How good is the potassium dichromate chemical oxygen demand method for determining organic pollutants in effluents?[3]

The majority of common organic compounds react completely when heated with an excess of potassium dichromate, making the method reliable and consistent (to ensure an excess of potassium dichromate a back titration is used *[Box 2]*).

Unfortunately, potassium dichromate also reacts with some oxidisable compounds that are not organic in nature and we must be aware of these interferences and errors if the COD measured is expected to represent the organic content of an effluent. There are a number of inorganic compounds that can react with potassium dichromate but only a limited number that are commonly encountered in natural waters and industrial effluent streams, namely, chloride, ferrous,

Table 2: Potassium dichromate COD interferences

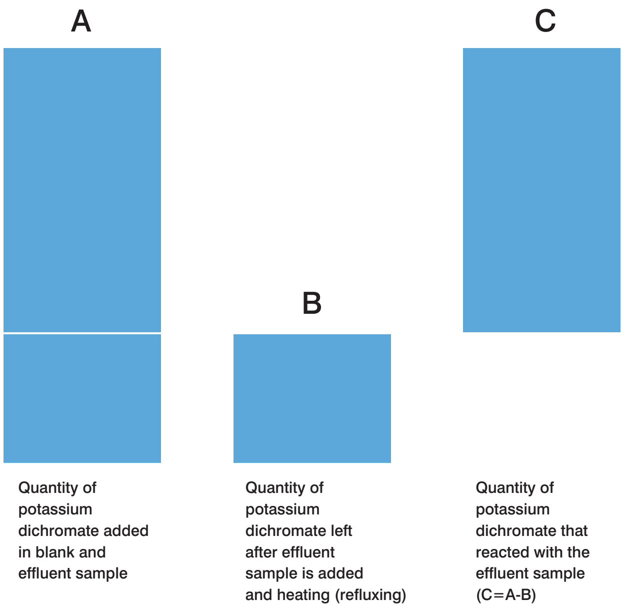
Interference	Elimination	Checks/Corrections
Chloride	Addition of mercuric sulfate to the analysis	Samples should be checked to ensure the amount of mercuric sulfate added is sufficient for high levels of chloride
Sulfide	None	The sulfide content of an effluent should be measured and a corrected value subtracted from the COD content to ensure that the COD reflects only the organic pollutants

Box 2 Potassium dichromate COD Back Titration[3]

A standard procedure to measure COD is described in the following.

A fixed amount of potassium dichromate is added to two flasks, respectively. Effluent sample is added to one flask only and distilled water to the other as a blank/reference. Care must be taken to ensure that the effluent sample added is small enough (or dilute enough) that it does not react with all of the potassium dichromate present to ensure that the potassium dichromate is in excess*.

Both samples are then heated (refluxed) for about two hours to encourage complete reaction of the potassium dichromate with the effluent sample. The amount of potassium dichromate present is then measured by titration and calculated for the distilled water blank/reference (A) and for the effluent sample (B). The amount of potassium dichromate that reacts with the effluent sample (C) is calculated by subtracting the effluent sample potassium dichromate result from the blank/reference (C=A-B). The amount of potassium dichromate that reacts (C) is then converted to a theoretical amount of oxygen provided to the sample. The analysis takes 5-8 hours to complete.



**Potassium dichromate is bright orange but when it reacts with organic compounds it changes to a green colour. To ensure that the potassium dichromate is in excess and for the back titration to work, the effluent sample must retain some orange colour after heating and cannot be completely green. If the sample goes green, the analysis needs to be repeated with a smaller effluent sample*

sulfide and nitrite ions. Nitrite and ferrous ions are not expected in tannery effluents, but precautions need to be exercised for chlorides and sulfides, as these pollutants are significant in selected effluent streams, e.g., sulfides in liming liquors and chlorides in soaking and pickle liquors. Sulfide and chloride ions react and are oxidised by potassium dichromate and give false positive results for organic pollutants *[Table 2]*.

Why is COD so important?

The COD and solids content of sewage and industrial effluents are two of the most important parameters used to calculate effluent treatment costs as illustrated by the Mogden Formula.[4] *[Box 3]* Many governments may also impose strict regulations on the COD levels of effluents discharged by factories.

Box 3 The Mogden Formula[4]

The Mogden formula, named after a sewage treatment plant in west London, UK, is commonly used as a basis to calculate the pricing of industrial effluent treatment. There are two effluent parameters used in the pricing for COD and suspended solids.

COD gives a reliable, accurate, consistent, convenient and relatively inexpensive representation of the overall polluting power of an effluent and therefore also provides an indication of how difficult or expensive it will be to treat the effluent.

The ratio of BOD_5 to COD values can be used to investigate the viability of biological treatments to treat an effluent. BOD_5 represents the biodegradable component of the oxygen demand and COD represents the maximum oxygen demand.

A BOD_5/COD ratio of 1 would indicate that a biological effluent plant could be used to eliminate all of the COD in 5 days. A BOD_5/COD ratio of 0 indicates that the organic components are not biodegradable at all. Tannery effluents will vary depending on the raw materials, processing methods and chemicals but will commonly have a BOD_5/COD ratio between 0.3-0.5.[5]

It is useful to note that biological effluent plants reduce aqueous COD by converting the organic material into biomass which increases the solid content of an effluent, hence effluent COD goes down but the effluent solids content also goes up.

Additional Oxygen Demands

Organic compounds commonly contain the elements carbon, hydrogen, oxygen and nitrogen. The potassium dichromate COD method accounts for the oxygen demand for carbon and hydrogen, but it does not measure the oxygen demand from nitrogen. To calculate a theoretical nitrogen oxygen demand, the TKN of an effluent (in mg/L) is frequently multiplied by a factor (usually 5) and added to the potassium dichromate COD to provide a total COD[3].

Total Organic Oxygen Demand

$$= COD_{carbon} + COD_{hydrogen} + COD_{oxygen} + COD_{nitrogen}$$

$$= COD_{potassium\ dichromate} + 5xTKN$$

Conclusions

COD is a direct measure of the amount of matter in an effluent that reacts (is oxidised) with potassium dichromate.

COD is a representation of the maximum amount of oxygen that may be required to neutralise the oxidisable pollutants in an effluent.

COD is commonly utilised to represent the amount of organic pollutants in an effluent.

COD is a reliable, reproducible, fast, convenient and affordable analytical technique.

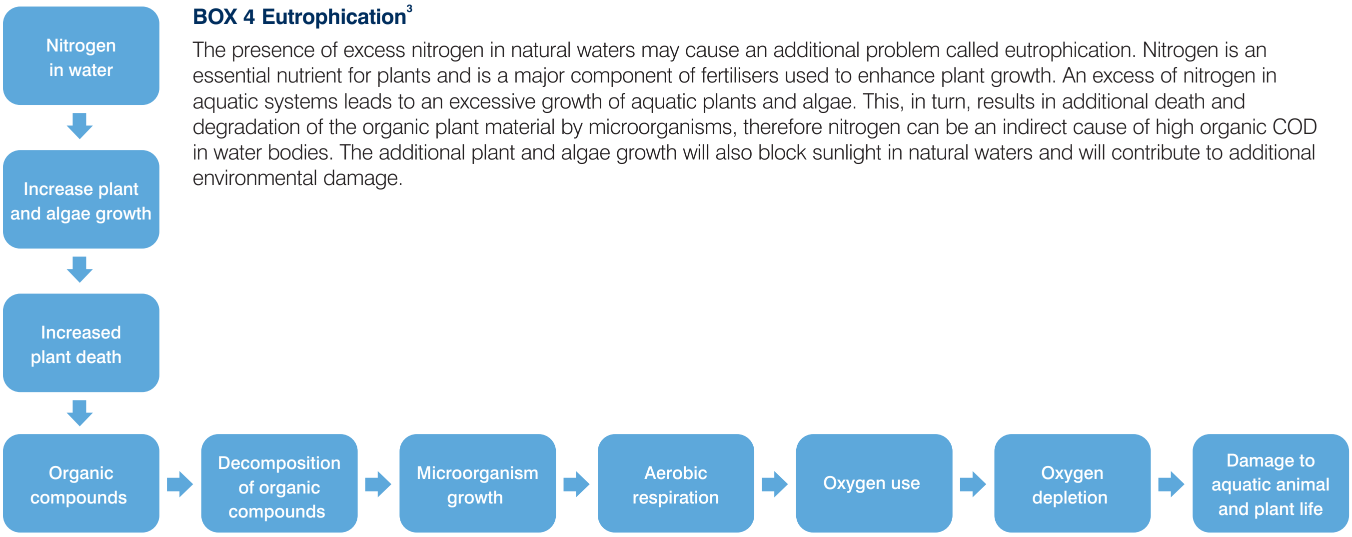
COD is a good indicator of the overall polluting power of an effluent and is therefore an extremely important parameter in wastewater analysis and effluent treatment processes.

References

1. *The Framework for Leather Manufacture, Volume III, World Trades Publishing Limited, 2013.*
2. *The American Chemical Society, www.acs.org, accessed March 2021.*
3. *Standard Method for the Examination of Water and Sewage, American Public Health Association, 2017.*
4. *Stephen Merrett, The Price of Water: Studies in Water Resource Economics and Management, London, 2005.*
5. *Best Available Techniques Reference Document for the Tanning of Hides and Skins, Industrial Emissions Directive 2010/75/EU, 2013.*

BOX 4 Eutrophication[3]

The presence of excess nitrogen in natural waters may cause an additional problem called eutrophication. Nitrogen is an essential nutrient for plants and is a major component of fertilisers used to enhance plant growth. An excess of nitrogen in aquatic systems leads to an excessive growth of aquatic plants and algae. This, in turn, results in additional death and degradation of the organic plant material by microorganisms, therefore nitrogen can be an indirect cause of high organic COD in water bodies. The additional plant and algae growth will also block sunlight in natural waters and will contribute to additional environmental damage.



Part Two: COD – chemical oxygen demand as a diagnostic tool

Dr Jeffry Guthrie-Strachan, Stephen Trantum, Ulrich Buckenmayer
Trumpler, Germany

The determination of chemical oxygen demand (COD) is a reliable, reproducible, fast, convenient, and affordable way of measuring the amount of organic matter in a sample of effluent (see Part 1: COD, World Leather, April/May 2021).

The conventional use of COD is to measure the amount of organic matter presented to the effluent plant in order to determine (i) how polluting the effluent is, (ii) how hard the effluent plant needs to work, (iii) what is required to treat the effluent and (iv) how well the effluent plant performs.[1]

While COD is such an important parameter in effluent analysis and costing, Trumpler decided to use COD analysis as a diagnostic tool to:

(A) understand the COD composition of its proprietary products,

(B) investigate the use of COD to determine the exhaustion of dyehouse products (retanning and fatliquoring agents), and

(C) use comprehensive experimentally determined COD data of proprietary and commodity leather chemicals to predict effluent COD loadings from practical dyehouse leather recipes.

A: The COD/organic composition of dyehouse proprietary products

Trumpler determines the COD content of its proprietary products as standard quality assurance practice, using a standard COD analysis (see Part 1: COD). The COD of a product depends on:

(i) the amount of organic material present in the product, which is directly linked to the active matter (AM), namely the non-water component of a product *(Box 1)*, and

(ii) the Inherent COD of a chemical, e.g., the degree to which the organic material is already oxidised *(Box 2)*.

The company determined the COD for more than 100 of its dyehouse products, including fatliquors, phenolic syntans and vegetable tannins, and resins and polymers. The COD of the individual products was measured and plotted against active matter *(Box 3)*. The data was then extrapolated to determine the COD based on a theoretical 100% active matter equivalent (AME) for each product, summarised in Table 1.

A product with high COD indicates:

- the product is predominantly organic in nature (fatliquors, phenolic syntans, vegetable tannins etc.), and/or
- the product has a high active matter, i.e., low water content (e.g., powder vegetable tannins and syntans and/or high active matter fatliquors, AM>90%)

A product with low COD indicates:

- the product is predominantly inorganic in nature (e.g., fillers and selected neutralising syntans etc.), and/or
- the product has a low active matter, i.e., high water content (e.g., acrylic syntans, AM=30-35%), and/or
- the product is organic but has a low inherent COD (e.g., acrylic syntans, formic acid etc.)

Therefore, the COD of a proprietary product should be expressed in terms of 100% AME in order to be compared directly with other products.

Products, such as fatliquors, are expected to have high CODs as fats and oils from natural sources are organic and have a high Inherent COD.

What is most important with all products is exhaustion.

Table 1: : A summary of Figures 3.1-3.3 (Box 3) showing the COD ranges for Trumpler retanning & dyehouse proprietary products based on their active matter and Inherent COD based on 100% active matter equivalent (AME).

Proprietary Products	Product COD Range (mg/g)	COD Range based on) on 100% AME (mg/g)	Inherent COD based on 100% AME (mg/g)
Fatliquors	826 (40% AM) to 2730 (100% AM)	2000-3000	2550
Retanning Agents & Vegetable Tannins	210 (35% AM) to 1500 (92% AM)	1200-1600	1500
Acrylic Syntans	250 (30% AM) to 491 (33% AM)	800-1500	990

Box 1 What is a proprietary product[2] and what is active matter?

Proprietary products contain one or more active ingredients and then a range of stabilisers, emulsifiers, and/or auxiliaries where required, and often water. The active ingredients, stabilisers, emulsifiers and auxiliaries may be organic (COD active), and/or inorganic in nature (COD inactive).
Water is found in most products, even powders, where it commonly makes up between 0 and 8% by mass (humidity and product dependent). Liquid products often vary between 0 and 70% water by mass. Table 1.1 summarises some typical active matter values expected for selected retanning and fatliquoring products.

Table 1.1: Typical active matter ranges for selected retanning and fatliquoring agents.

Product	Typical Active Matter Ranges
Syntans, Vegetable Tannins (powder)	>90%
Acrylic Syntans (liquid)	30-35%
Fatliquors (high AM)	>90%
Fatliquors (low AM)	40-50%
Syntans (liquid)	40-70%

Trumpler considers the active matter (AM) in powder products to be the dry matter (after heating at 105°C and determined gravimetrically) and in liquid/paste products the AM is determined as the non-water content (the water content of a product is determined using the Karl-Fischer titration). For this investigation, AM includes active ingredients, stabilisers, emulsifiers and auxiliaries *(Figure 1.1)*.

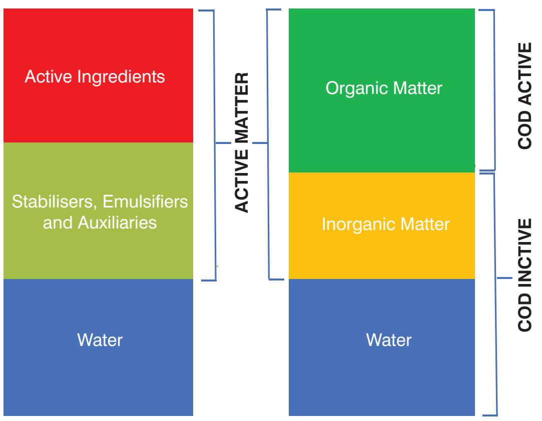


Figure 1.1: Generic representation of the composition of proprietary products indicating active matter and COD activity.

If a product has a high COD but exhausts very well it is likely to contribute to less COD in the effluent than a low COD product that does not exhaust well.

Trumpler considered the use of COD as a tool to measure the exhaustion of its proprietary dyehouse chemicals.

B: The exhaustion of Trumpler dyehouse products utilising COD

With the aid of a simple mass balance, it can be understood that the total organic matter (TOM) comprises the endemic organic matter (EOM) *(Box 4)* and the added organic matter (AOM) according to Equation 1. The AOM will either bind/fix to the chrome-tanned collagen matrix or it will not bind/fix and is drained out of the drum and heads to the effluent plant (Equation 3). If we assume that the amount of EOM remains constant, we can further deduce that the amount of bound organic matter can be determined according to Equation 4 using the COD of the AOM (measured in Section A for each individual product) and the COD of the unbound organic matter (float COD) after processing.

Total Organic Matter = Endemic Organic Matter + Added Organic Matter *(Equation 1)*

Total Organic Matter = Endemic Organic Matter + Bound Organic Matter + Unbound Organic Matter *(Equation 2)*

Added Organic Matter = Bound Organic Matter + Unbound Organic Matter *(Equation 3)*

Bound Organic Matter = Added Organic Matter – Unbound Organic Matter *(Equation 4)*

Box 2 The inherent COD of organic matter

The degree to which organic matter is oxidised has a significant effect on the inherent COD of an organic material. The COD analysis process actually determines the amount of oxygen required to oxidise an organic material completely to carbon dioxide and water according to Equation 2.1*(see World Leather April-May Part 1)*.

$$C_xH_y + (x+\tfrac{y}{4})O_2 \rightarrow xCO_2 + \tfrac{y}{2}H_2O \text{ (Equation 2.1)}$$

So, for an unoxidised chemical (when x = 2 and y = 6) called ethane:

$$C_2H_6 + 3\tfrac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O \text{ (Equation 2.2)}$$

And for a highly oxidised chemical (when x = 2 and y = 2, with 4 oxygens) called oxalic acid:

$$C_2H_2O_4 + \tfrac{1}{2}O_2 \rightarrow 2CO_2 + H_2O \text{ (Equation 2.3)}$$

Thus, to oxidise one molecule of ethane requires 3.5 oxygen molecules and to oxidise one molecule of oxalic acid requires half a molecule of oxygen. This means that it takes 7 times more oxygen to oxidise ethane than it takes to oxidise oxalic acid, therefore, the COD of ethane is 7 times higher than the COD of oxalic acid even though both materials are organic.
Trumpler calculated the theoretical inherent COD of several chemicals *(Figure 2.1)*. From Figure 2.1 we can determine that the highest inherent organic COD possible is 4000mg/g for methane (CH_4) and the lowest possible inherent organic COD is 178mg/g for oxalic acid ($C_2H_2O_4$).
As an organic molecule gets bigger, with longer carbon chains, the inherent COD increases to between 2500 and 3500 mg/g (except for hydrocarbons that decrease from 4000 to 3500mg/g). Finally, as an organic molecule has additional groups added to the chain the COD decreases according to hydrocarbons > mono-alcohols > di-alcohols > mono-carboxylic acids > di-carboxylic acids.
The inherent COD of fatliquors, retanning agents and acrylic syntans can be determined from the average 100% active matter equivalents (AME) in this study.

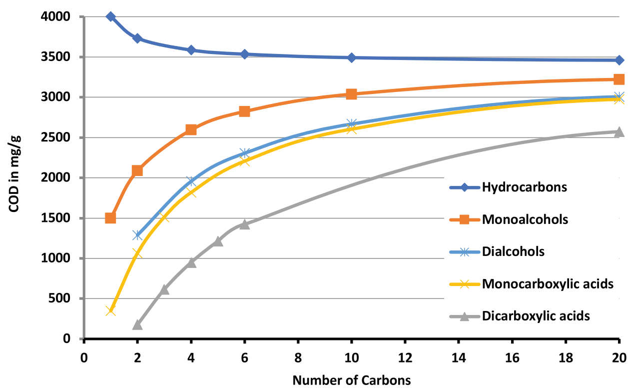


Figure 2.1: A graph representing theoretically calculated inherent COD values for a range of simple organic molecules with chains up to 20 carbons long.

Box 3 Proprietary product COD vs active matter and inherent COD for fatliquors, retanning agents and acrylic syntans

The graphs show the relationship between active matter and COD and the 100% active matter equivalent (AME) for fatliquors (●, *Figure 3.1*), phenolic syntans (▲, *Figure 3.2*) and acrylic syntans (♦, *Figure 3.3*). The units of mg O_2/g indicate the mass of oxygen (in mg) that would theoretically be required to completely 'neutralise' 1 gram of the product, i.e., the oxygen demand per gram of product.

Fatliquors ●

Fatliquors are generally 100% organic in nature with a high inherent COD, therefore the products integrate well in Figure 3.1 to provide a linear trendline when plotting COD vs AM. The inherent COD of fatliquors is represented by the average 100% AME for fatliquors of 2550mg O_2/g.

Retanning agents ▲

Retanning agents may be 100% organic but are often blended with inorganic powders for a number of practical reasons and this results in a more complicated picture. The results in Figure 3.2 fall into three categories, namely,

(i) fully organic phenolic retanning agents (▲) with 100% AME ranging from 1330-1630mg/g. These products integrate well and provide a linear trendline when plotting COD vs AM. The inherent COD of fully organic retanning agents is represented by the average 100% AME of 1500mg O_2/g.

(ii) High AM organic/Inorganic retanning agents (▲) with 100% AME ranging from 800-1200mg/g. The products have a moderate inorganic content and organic components with low inherent COD. Products tend to be neutralising syntans and polymeric retanning agents.

(iii) High AM Inorganic/organic syntans (▲) with 100% AME ranging from 130-700mg/g. These products tend to have a high inorganic content and organic components with a low inherent COD, such as neutralising syntans and filling agents.

Acrylic Syntans ♦

Acrylic syntans are generally 100% organic in nature and completely COD active, therefore the products integrate well in Figure 3.3 to provide a linear trendline when plotting COD vs AM. The inherent COD of acrylic syntans is represented by the average 100% AME for acrylic syntans of 990mg O_2/g.

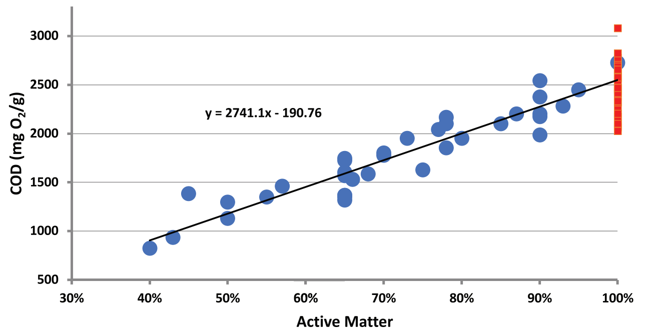


Figure 3.1: Graph showing fatliquor (•) product COD (mg/g) versus active matter (AM) (including 100% AME,▪). The average 100% AME for fatliquors is 2550mg/g.

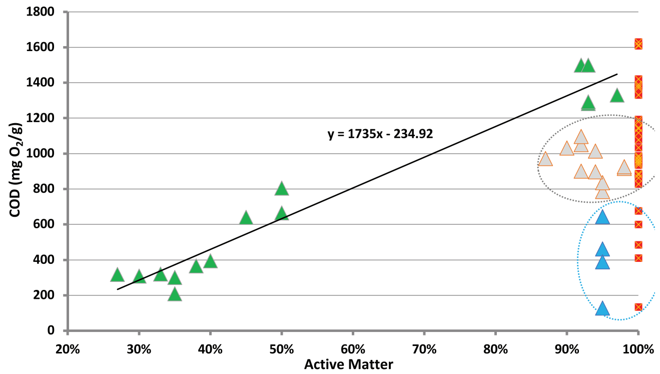


Figure 3.2: Graph showing retanning agents (▲) proprietary product COD (mg/g) versus active matter (AM) (including 100% AME,▪). The average 100% AME for fully organic retanning agents is 1500mg/g.

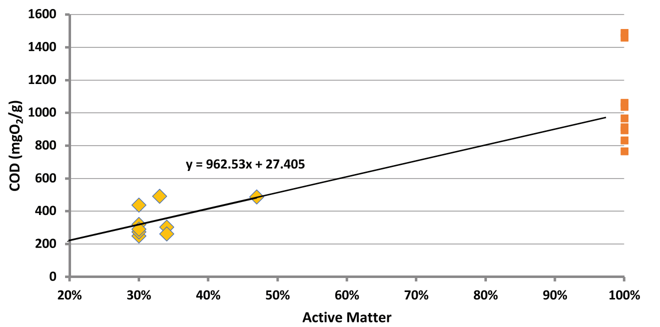


Figure 3.3: Graph showing acrylic syntan (♦) proprietary product COD (mg/g) versus active matter (AM) (including 100% AME,▪). The average 100% AME for acrylic syntans is 990mg/g.

Experimental design – product exhaustion

Trumpler conducted a number of experiments in an effort to determine viable product offers (*Table 2*), product processing conditions, and practical recipes in accordance with standard leather manufacturing processing parameters.

Wet blue was used from the same supplier and the same batch wherever possible. Every hide that was processed was divided into 12 samples, including two internal blank samples to eliminate interferences arising from EOM.

Wet blue hides were prepared and processed according to standardised recipes and procedures developed for the investigation *(Appendix 1: Recipes 1, 2 & 3)*. In addition, the blank samples were processed under the same experimental conditions, times and chemical offers without the proprietary products, to eliminate any interferences due to products not under investigation. This allowed the experiments to isolate the effect of the proprietary products and determine the COD of the unbound organic matter according to Equation 5. The exhaustion of the individual proprietary products could then be determined according to Equation 6.

Table 2: Product offers determined experimentally based on 100% Active Matter Equivalent (AME)

Product	Product Offer based on 100% AM Equivalent
Fatliquors	7%
Retanning Agents & Vegetable Tannins	8%
Acrylic Syntans	1.8%

APPENDIX 1: Exhaustion study recipes for fatliquors (Recipe 1), retanning agents (Recipe 2) and acrylic syntans (Recipe 3)

Recipe 1: Standard recipe for Fatliquor product exhaustion investigation.

Process	%	Product	T (°C)	Time	Comments
		12 Samples Processed Together			
Neutralisation	300	Water	35		
	2	Sodium formate		20'	
	0.3	Sodium bicarbonate		40'	pH 5.2-5.5 (Ø BCG)
Retanning	3	Acrylic Syntan (1:3)		30'	
	6	Phenolic Syntan		60'	Drain
Wash	300	Water	60	15'	Drain
		Samples separated and processed individually			
Fatliquoring	200	Water	60		
	7*	**FATLIQUOR (1:3)**		**60'**	**Blank = no fatliquor**
Fixing	1	Formic acid (1:10)	20	40'	pH 3.4-3.8
		Sample of float removed for COD analysis			
Wash	300	Water	20	15'	

** Based on 100% AME. A fatliquor with AM of 50% would require an actual offer of 14%.*

Recipe 2: Standard recipe for retanning agent product exhaustion investigation.

Process	%	Product	T (°C)	Time	Comments
		12 Samples Processed Together			
Neutralisation	300	Water	35		
	2	Sodium formate		20'	
	0.3	Sodium bicarbonate		40'	pH 5.2-5.5 (Ø BCG)
Wash	300	Water	60	15'	
		Samples separated and processed individually			
Retanning	3	Acrylic Syntan (1:3)		30'	
	8*	**RETANNING AGENT**		**60'**	**Blank = no veg/phenolic syntan**
Fatliquoring	200	Water	60		
	7	Fatliquor (1:3)		60'	
Fixing	1	Formic acid (1:10)	20	40'	pH 3.4-3.8
		Sample of float removed for COD analysis			
Wash	300	Water	20	15'	

** Based on 100% AME. A retanning agent with AM of 90% would require an actual offer of 8.9%.*

Recipe 3: Standard recipe for acrylic syntan product exhaustion investigation.

Process	%	Product	T (°C)	Time	Comments
		12 Samples Processed Together			
Neutralisation	300	Water	35		
	2	Sodium formate		20'	
	0.3	Sodium bicarbonate		40'	pH 5.2-5.5 (Ø BCG)
Wash	300	Water	60	15'	
		Samples separated and processed individually			
Retanning	**1.8***	**ACRYLIC SYNTAN (1:3)**		**30'**	**Blank = no acrylic syntan**
	6	Phenolic Syntan		60'	
Fatliquoring	200	Water	60		
	7	Fatliquor (1:3)		60'	
Fixing	1	Formic acid (1:10)	20	40'	pH 3.4-3.8
		Sample of float removed for COD analysis			
Wash	300	Water	20	15'	

** Based on 100% AME. An acrylic syntan with AM of 30% would require an actual offer of 6%.*

Unbound Organic Matter COD = Proprietary Product Float COD – Blank Float COD *(Equation 5)*

% Exhaustion = Proprietary Product $\frac{\text{(Bound Product COD)}}{\text{(Added Product COD)}}$ x 100 *(Equation 6)*

The results for the exhaustion of products can be viewed in Figures 5.1-5.3 *(Box 5)*.

Discussion

At the beginning of the study, the hypothesis was that fatliquors with a lower AM would have lower exhaustions due to the need for extra emulsifiers and stabilisers. This, however, is not evident based on the results. Generally, fatliquor exhaustion is high to almost complete based on 7% offer at 100% AME with most exhaustions above 90%. One low AM fatliquor exhibited an almost complete exhaustion of 98%.

The almost complete exhaustion fatliquors (>98%) tended to be fish oil-based with very low emulsifier and stabilizer requirements.

The moderate exhaustion product with 74.5% exhaustion was not unexpected as it is a cationic fatliquor and exhaustion was predictably lower.

The fatliquor results showed excellent correlations between duplicate and similar products.

The results for the retanning agents were a bit more complicated as the products are significantly more diverse. There are liquid and powder products, as well as vegetable tannins, phenolic syntans, naphthalene-based neutralizing syntans, collagen-hydrolysates, and melamine-based filling resins.

The vegetable tannins, phenolic syntans and collagen hydrolysates exhibited moderate to high exhaustions illustrated by the 70-90% exhaustion results *(▲&▲Figure 5.2)*.

Products containing components with reduced binding capacity, e.g., naphthalene sulphone condensate-based neutralising agents, gave somewhat lower levels of exhaustion, as expected.

The acrylic syntans delivered with very high to almost complete exhaustions across the board (93-100% exhaustion) based on 1.8% at 100% AME. The offer of 1.8% for a 30% AM product equates to an actual offer of 6% which is in line with industry expectations. Industry norms for acrylic syntan offers vary from 2-4% for European hides up to 10% for South American material.

All the data gathered for the individual products was combined with COD data for commodity products in an effort to predict the effluent COD values of standardised recipes.

C: Prediction of effluent COD values

Imagine if one could design a recipe and, with the click of a button, predict the effluent COD that would be produced. It would be an invaluable tool in the formulation of low COD recipes if it were possible. Trumpler decided to use the extensive COD data generated from this project and investigate how accurate effluent COD predictions could be.

.

Experimental design – COD prediction

Standard recipes were developed in accordance with those for the exhaustion experiment based on 100% AME of 8% retanning agent and 7.5% fatliquor. The retanning agent and fatliquor offers comprised three products each. Due to the extremely high exhaustion of acrylic syntans the acrylic offer was fixed at 5% for all experiments.

Box 4 Endemic and added organic material in hides, skins and leather manufacture

In leather manufacture, the beamhouse operations remove undesirable materials from the hide or skin and leave collagen, elastin and other residual components behind in a natural, fibrous, collagen matrix. This is why the beamhouse processes generate effluents with significant COD loadings *(Figure 4.1)* as fats, hair and other components have a high Inherent COD. Tanning, retanning and dyehouse operations, stabilise the collagen matrix and then fill it with the required chemicals in the desired amounts to provide the base colour and properties required of the final leather. Many of the retanning and dyehouse products added are also COD active.

Table 4.1: Endemic organic matter for raw hides and wet blue and added organic matter in retanning, dyeing & fatliquoring

Endemic Organic Matter(Raw Hides)	Endemic Organic Matter (Wet Blue)	Added Organic Matter in Retanning and Dyehouse
Collagen	Collagen (80%)	Vegetable Tannins
Keratin (hair, epidermis)	Elastin	Syntans
Elastin	Residual Fats	Fatliquors
Natural Proteins	Residual Proteins	Dyestuffs
Fats		Formic acid/Formate
Natural Sugars		Resins & Polymers

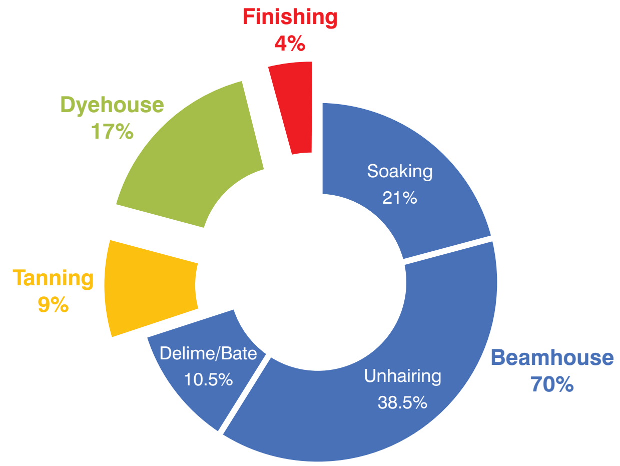


Figure 4.1: Generic COD effluent contributions according to leather manufacturing stages/processes.[3]

The experiments were designed to look at fatliquors *(Appendix 2: Recipes 4 & 5)* and retanning agents *(Appendix 2: Recipes 6 & 7)* independently but also to investigate the potential for synergistic and antagonistic effects for high exhaustion products *(Recipe 4 & 6)* and for moderate/poor exhaustion products *(Recipes 5 & 7)*. The predicted COD was calculated using individual product and chemical COD data and the amount of water used. Samples were removed and sent for analysis to compare with the calculated values. The results are summarised in *Table 3*.

Discussion

The exhaustion studies produced results that were a great deal closer than initially expected. It must be understood that COD variations of 5% are not unexpected and that a difference in COD of ±2550mg/L may equate to an equivalent difference of ±1g/L of a 100% AME fatliquor.

As suspected, products that exhaust well have a synergistic effect on other products and both high exhaustion product experiments resulted in measured effluent CODs that were

APPENDIX 2: COD prediction study recipes for fatliquors (Recipes 4 & 5) and retanning agents (Recipes 6 & 7)

The % Active Matter refers to the AM for the individual product and the Exhaustion % is the exhaustion value measured for each product in Part B of this exercise (AM%/Exhaustion%).

Recipe 4: Standard recipe for COD prediction study using high exhaustion fatliquors (A, B & C) including chemical active matter (AM) and exhaustions (AM%/Exhaustion%).

Process	%	Product	T (°C)	Time	Comments
Wet Back	100	Water	20		
Retanning	5	Acrylic Syntan (30%/96%)		20’	Dilute 1:3
	2*	Retanning Agent 1 (35%/87%)		20’	
	3*	Retanning Agent 2 (95%/78%)		20’	
	3*	Retanning Agent 3 (94%/87%)		60’	
Fatliquoring	100	Water	60		
	2.5*	**FATLIQUOR A (90%/98.9%)**			
	2.5*	**FATLIQUOR B (95%/98.2%)**			
	2.5*	**FATLIQUOR C (85%/98.5%)**	60	90’	Blend & dilute 1:4
Fix	2x1	Formic acid (70%/5%)		40’	Dilute 1:10
		Sample Collected for Analysis			

** Based on 100% AM equivalent*

Recipe 5: Standard recipe for COD prediction study using moderate/high exhaustion fatliquors (D, E & F) including chemical active matter (AM) and exhaustions (AM%/Exhaustion%)

Process	%	Product	T (°C)	Time	Comments
Wet Back	100	Water	20		
Retanning	5	Acrylic Syntan (30%/96%)		20’	Dilute 1:3
	2*	Retanning Agent 1 (35%/87%)		20’	
	3*	Retanning Agent 2 (95%/78%)		20’	
	3*	Retanning Agent 3 (94%/87%)		60’	
Fatliquoring	100	Water	60		
	2.5*	**FATLIQUOR D (70%/88.9%)**			
	2.5*	**FATLIQUOR E (65%/87.0%)**			
	2.5*	**FATLIQUOR F (65%/86.3%)**	60	90’	Blend & dilute 1:4
Fix	2x1	Formic acid (70%/5%)		40’	Dilute 1:10
		Sample Collected for Analysis			

** Based on 100% AM equivalent*

Recipe 6: Standard recipe for COD prediction study using high exhaustion phenolic syntans (α, β & γ) including chemical active matter (AM) and exhaustions (AM/Exhaustion%)

Process	%	Product	T (°C)	Time	Comments
Wet Back	100	Water	20		
Retanning	5	Acrylic (30%/96%)		20’	Dilute 1:3
	2*	**RETANNING AGENT α (35%/87%)**		20’	
	3*	**RETANNING AGENT β (95%/78%)**		20’	
	3*	**RETANNING AGENT γ (94%/87%)**		60’	
Fatliquoring	100	Water	60		
	7.5*	Fatliquor (90%/98.2%)	60	90’	Dilute 1:4
Fix	2x1	Formic acid (70%/5%)		40’	Dilute 1:10
		Sample Collected for Analysis			

** Based on 100% AM equivalent*

Recipe 7: Standard recipe for COD prediction study using moderate/high & poor exhaustion phenolic syntans (δ, ε & σ) including chemical active matter (AM) and exhaustion (AM%/Exhaustion%)

Process	%	Product	T (°C)	Time	Comments
Wet Back	100	Water	20		
Retanning	5	Acrylic (30%/96%)		20’	Dilute 1:3
	2*	**RETANNING AGENT α (27%/44%)**		20’	
	3*	**RETANNING AGENT β (98%/8%)**		20’	
	3*	**RETANNING AGENT γ (92%/77%)**		60’	
Fatliquoring	100	Water	60		
	7.5*	Fatliquor (90%/98.2%)	60	90’	Dilute 1:4
Fix	2x1	Formic acid (70%/5%)		40’	Dilute 1:10
		Sample Collected for Analysis			

** Based on 100% AM equivalent*

Box 5: Exhaustion study results for fatliquors (●), phenolic syntans (▲) and acrylic syntans (♦)

The results from the exhaustion study utlising fatliquors (●, *Figure 5.1, Recipe 1*), retanning agents (▲, *Figure 5.2, Recipe 2*) and acrylic syntans (♦, *Figure 5.3, Recipe 3*). Please note that the exhaustion measured in this study is based on organic COD active material. The exhaustion of inorganic or COD inactive components is not represented or measured in this exercise.

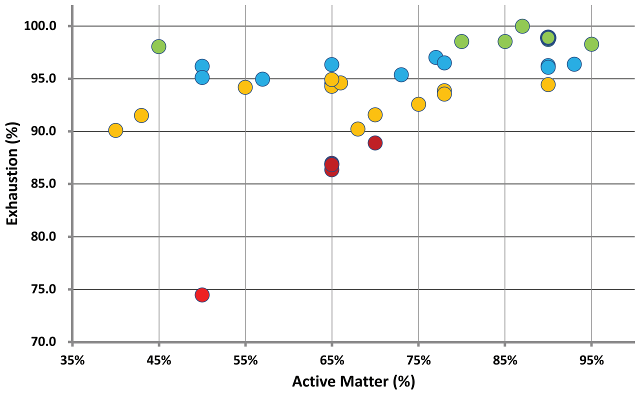


Figure 5.1: The exhaustion of proprietary fatliquor products versus their active matter (AM). Exhaustion results were arranged into four categories, (i) Almost Complete Exhaustion,, >98% (●), (ii) Extremely High Exhaustion, 95-98% (●), (iii) Very High Exhaustion, 90-95% (●), and High Exhaustion, 85-90% (●). One product (●), a cationic fatliquor, stands out with an expected Moderate Exhaustion of 74.5%.

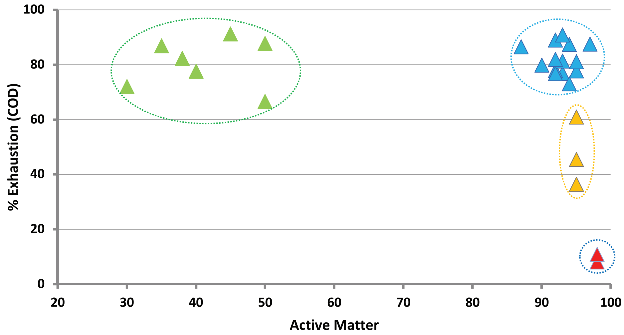


Figure 5.2: The exhaustion of proprietary retanning agents versus their active matter (AM). Exhaustion results fall into four apparent categories, (i) Low AM – Moderate to High Exhaustion (▲), (ii) High AM – Moderate to High Exhaustion (▲), (iii) High AM – Moderate to Poor Exhaustion (▲), and (iv) High AM – Poor Exhaustion (▲).

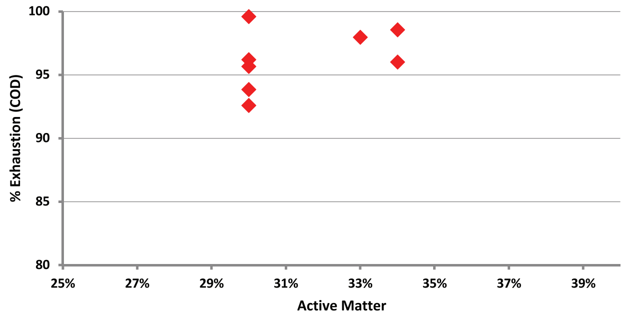


Figure 5.3: The exhaustion of proprietary acrylic syntans (♦) versus active matter (AM). All products exhaust to a very high amount or almost complete.

Table 3: Results for the COD prediction study for fatliquors and retanning agents using using high exhaustion and moderate/poor exhaustion products.

Products Investigated	Recipe	Product Exhaustion	COD predicted (mg/L)	COD measured (mg/L)	COD measured Vs COD Predicted)
Fatliquors	4	High	7 546	5 770	23.5% lower
	5	Moderate	14 053	13 580	3.4% lower
Retanning Agents	6	High	7 878	6595	16.3% lower
	7	Moderate/Poor	22 648	26 451	16.8% higher

lower than expected, 23.5% and 16.3% respectively.

Moderate and poor exhaustion products produced measured COD results that were close to expected and higher than expected, illustrating the potential of an antagonistic effect.

The results show great promise for the prediction of effluent COD when using simple recipes and may be easily applied to production systems that rely on large volume production cycles. Modifications and changes to the recipe can be reliably measured and followed using COD as a diagnostic tool.

Conclusions

Leather manufacture is an incredibly complicated process with multiple products and process parameters, without even considering the variety of raw materials. A deeper understanding of COD and its contributions goes a long way to provide a better picture of what is happening between chemical products in the drum, the leather and what goes down the drain to the effluent. COD is an effective tool for the tanner's arsenal.

As a diagnostic tool, COD can be effectively used to understand the COD contributing components of individual proprietary products.

The individual COD data for each proprietary product can be applied to the measurement of individual product exhaustions using standardised recipes.

The exhaustion COD data for each individual product can be successfully combined with other product data in simple standardised recipes to predict effluent CODs and shows better than expected correlation with measured data. Synergistic and antagonistic effects are demonstrated between product groups.

References

J.J. Guthrie-Strachan, S.R. Trantum & Ulrich Buckenmayer, Part 1: COD: What is Chemical Oxygen Demand?, World Leather, April/May 2021, Pg 28-31.

1. *R. Daniels, The Framework for Leather Manufacture, Volume III, World Trades' Publishing Ltd, 2013.*
2. *Proprietary Material, www.lawinsider.com/dictionary/, accessed 20.06.2021.*
3. *Best Available Techniques Reference Document for the Tanning of Hides and Skins, Industrial Emissions Directive 2010/75/EU, 2013.*

Acknowledgements:

Trumpler would like to thank the following people for their significant contributions in the processing, measurement and generation of data that made this study possible: Christiane Schiefer, Andreas Frank, and Simone Heymann and her team.