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Copper (Cu) as a Possible Inhibitor from the Interferences of Sulphur during Analysis of Organochlorines

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Abstract
In chemical and environmental analyses, there are interferences that could affect the qualitative and quantitative results of such analyses. A typical example is the analysis of Organochlorinesin soil that can contain anaerobic sulphur in considerable quantity. Sulphur is highly responsive to Electron Capture Detector (ECD) which in turn represents such interferences as massive peaks in spectra. In this work, Cu was introduced into different organochlorines(OCs) pesticides standards with different concentrations (50 ng, 100 ng and 150 ng) in order to remove the sulphur component. The results showed that the introduction of Cu into the analytes circumvented the effect of the sulphur on the samples with almost 100% recovery of the samples after the analyses. However, only a few of the OCsp,p-DDT and methoxychlor gave lower percentage recovery of 47 and 50% respectively for the 100 ng samples. The data obtained shows that the use of copper fillings / cuttings for pre-analytical sample treatment for alltwenty-six OCs tested with exception of two compounds showed acceptable recovery levels of >80%.

Keywords: **Organochlorines, copper, sulphur, electron capture detector.**

1. Introduction

The chemistry of reaction of sulphur (non-metal) and copper (a metal) is an interesting one which is applied in different industrial areas, foods and beverages, pesticides and herbicides and so on. In wine making, there is presence of sulphur which gives some reductive reactions or unplesant aromas which can be removed by introducing copper (Muller and Rauhut,2018). In pesticides, elemental sulfur finds great application in fighting diseases (Rauhut and Kurbel,1994; Rauhut 2017). These sulphur compounds are not inert and could interfer with other components to form undesirable compounds. It has been widely observed that in the analysis of soil and industrial samples for organochlorines, the presence of sulphur in the extract can greatly affect both the qualitative and quantitative analysis.

Sulfur can come from rocks and minerals which is released during weathering by water, temperature and chemical reactions. When sulfur is exposed to the air, it combines with oxygen and becomes the plant-available form; sulfate. Raw organic materials and humus are the sulfur storehouse in most soils.

Sulfur in the soil occurs in two basic forms, organic and inorganic S. The organic form accounts for 95 % of S in most soils. (Rossete et al, 2008).

Sulphur reducing bacteria are microorganisms that have the ability to reduce elemental sulphur (S_0) to hydrogen sulphide (H_2S). These microbes use inorganic sulphur compounds as electron acceptors to sustain several activities such as respiration, conserving energy and growth, in absence of oxygen. It is the product of sulphide (H_2S) that is now observed during analysis of the soil samples.These are some of the sources of the massive sulphur signals observed during analysis using Electron capture detector (ECD).

Electron capture detector (ECD) is one of the most important detector for the analysis of organochlorines due to its specificity, sensitivity and affinity for halogens and also very responsive to sulphur. The presence of the sulfur compounds in samples can cause catalyst deactivation, corrosion of equipment, and finally lead to reduction of product quality (Li et al,2015).
There are materials that can be used for the removal of sulfur compounds which includes activated carbon, metal organic frameworks and zeolites (Jiang et al,2003; Zhou et al,2006; Oliveiraa et al, 2009; Peralta et al,2012; Dai et al, 2013) . However, Cu is used in this work in order to avoid elaborate process and explore efficiency of the method over other materials. very simple, efficient, easy to maintain and do not interfere with the analytes.The aim of this work therefore is to ascertain if copper can be used in the prevention of interferences of sulphur during the analysis of organochlorines.

2. Materials and Method

2.1 Materials

Copper fillings or pellets obtained from Sigma Aldrich chemicals was used in extracting sulphur from the organochlorine pesticides, Quality control (QC) standard (EPA CLP Organochlorine Pesticide Mix) Supelco were standard pesticides used for this analysis.

2.2 Method

Different solutions of OCs were prepared at varying concentrations. QCC, QCD and QCE direct standard arein concentrations of 50ng, 100ng and 300ng respectively. The standard OCs used are: α-Hexachlorocyclohexane (α-HCH), 6Cl-Benzol, b-HCH, c-HCH, e-HCH, Heptachlor, Aldrin, Isodrin, c-Heptachlor, Oxychlordan, t-Heptachlor, c-Chlordan, o,p-dichlorodiphenyldichloroethylene (o,p-DDE), α-Endosulfan, t-Chlordan, Dieldrin, p,p-DDE, o,p-dichlorophenyldichloroethane (o,p-DDD), Endrin, b-Endosulfan, p,p-DDD, o,p-dichlorodiphenyltrichloroethane (o,p-DDT), Methoxychlor, Mrex, PCB 209. Copper pellets were then added accordingly: QCC + copper, QCD + copper and QCE + copper and a 48-hour reaction time for the QCs standards and the copper pellets was allowed. As the reactions proceeds the copper pellets changes their polished copper brightness and becomes more army greenish or even black. Depending on the amount of sulphur present in the samples, more copper is added or more time is given for reaction.

3. Results and Discussion

The presence of sulphur in soil and industrial samples affects the results of organochlorines (OCs) analysis. These sulphur componentsappear as peaks in the FID spectra thereby affecting the quality or results of the analysis. There were many sulphur signals observed in the chromatograms but the signals disappeared with the addition of copper pellets. Table 1 shows the quality tests of different organochlorines compounds at different concentrations (50 ng,100ng and 150 ng). The tests were conducted with and without copper. The different quality control (QC) concentrations are named QCC (50 ng), QCD (100 ng) and QCE (150 ng).The percentage recovery of the OCs compounds was also represented in Table 1 for the different concentrations after the introduction of the copper.

All the OCs gave percentage recovery of over 100 in the QCC, which reflects some type of machine or human error but means there was efficient recovery of the OCs after the introduction of copper. In QCD, o,p-DDT gave the lowest percentage recovery of 47% followed by methoxychlor with 50% recovery. In QCE, the recovery rate was high with methoxychlor and b-HCH having lowest recovery percentage of 84 and 85% respectively.

Table 1: Chlorpestizide QC's reacted with copper and recovery recovery of QC's standard

Probenbezeichnung	QCC	QCC	QCD	QCD	QCE	QCE	QCC	QCD	QCE
auf istd (10) berechnet		Copper		Copper		Copper	Recovery	Recovery	Recovery
a-HCH	56	62	91	95	334	298	111	104	89
6CL-Benzol	41	46	71	81	244	259	112	114	106
b-HCH	53	56	92	84	301	262	106	91	87
c-HCH	49	59	97	92	328	279	120	95	85
d-HCH	49	63	103	94	317	287	129	91	91
e-HCH	48	56	101	87	327	284	117	86	87
Heptachlor	36	39	52	58	226	207	108	98	92
Aldrin	56	67	100	97	340	293	120	97	86
Isodrin	54	61	95	96	319	297	113	101	93
c-Heptachlor	48	58	91	89	311	267	121	98	86
Oxychlordan	48	51	79	86	286	251	106	109	88
t-Heptachlor	55	61	103	95	311	279	111	92	90
c-Chlordan	45	51	91	83	275	260	113	91	95
o,p-DDE	52	65	107	95	319	296	125	89	93
a-Endosulfan	55	67	100	105	312	298	122	105	96
t-Chlordan	48	55	92	85	289	264	115	92	91
Diedrin	46	79	101	98	309	271	172	97	88
p,p-dde	45	58	102	84	281	261	129	82	93
o,p-DDD	43	58	102	86	280	256	135	84	91
Endrin	43	54	101	84	288	279	126	83	97
b-Endosulfan	47	52	97	88	264	247	111	91	94
p,p-DDD	39	51	106	82	259	239	131	77	92
o,p-DDT	51	51	130	87	320	284	100	67	89
p,p-DDT	33	40	148	70	332	287	121	47	86
Methoxychlor	23	29	114	57	261	220	126	50	84
Mirex	45	50	109	84	287	253	111	77	88
PCB 209	39	47	125	86	267	240	121	69	90

Discussion

In order to avoid the sulfur interference during analysis when using a GC coupled with an ECD detector, the extracts were treated with copper pellets and allowed to react for a while, depending on the level of sulphur present. Copper is a strong metal activator that easily complexes with sulphur containing compounds, however, in previous studies, there are doubts to the level of complexation with sulphur compounds (shahbaz 2011). More copper pellets were used and more time allowed for the copper to react with the entire sulphur present in the extract before the analysis.

Copper reacts with sulfur to form copper sulphide as follows: Cu + H_2S -----→ CuS + H_2O, the CuS was then precipitated out. The Cu-S bond is covalent in character with complex electronic band structures due to ease of electron delocalization. The simple chemistry involved in the bonding

of Cu with S is just polarization; Cu^{2+} cation which is highly polarizing withdraws electrons from S^{2-} anion which is highly polarizable.
Moreover, there exists some antagonisms between Cu and other microminerals leading to their low reactions or interactions (Espinosa et al.,2021) . The increase in reaction pH is also another way of precipitating insoluble Cu compounds and making them unavailble for reaction.

Conclusion

There are latent sources of sulphur in some samples such as organonochlorines which could be removed by introduction of copper pellets. The removal of sulphur interferences in analytes is such an interesting chemistry because the presence of sulphur in samples affects the qualitative analysis and gives results that are not reliable. Copper was introduced into some standard organochlorines samples in order to remove some elements of sulphur in them. At the end, the OCs were almost completely recovered except for the few standards of 100 ng where p,p-DDt and methoxychlor gave percentage recovery of 47% and 50% respectively. This work therefore has shown that introducing copper into organochlorine pesticdes can selectively remove sulphur and precipitate it as CuS without interfering with the compounds. This procedure will therefore give ECD results devoid of sulphur peaks and with higher accuracy.

References

Dai, W., Hu, J., Zhou, L., Li, S., Hu, X., Huang, H. (2013). Removal of Dibenzothiophene with Composite Adsorbent MOF-5/Cu(I) *Energy Fuels*, 27: 816−821.

Espinosa, C.D., Stein, H.H., (2021). Digestibility and metabolism of copper in diets for pigs and influence of dietary copper on growth performance, intestinal health, and overall immune status: a review. *J Animal Sci Biotechnol***12(**13) https://doi.org/10.1186/s40104-020-00533-3

Jiang, Z., Liu, Y., Sun, X., Tian, F., Sun, F., Liang, C., You, W., Han, C., Li, C. (2003).Activated Carbons Chemically Modified by Concentrated H_2SO_4 for the Adsorption of the Pollutants from Wastewater and the Dibenzothiophene from Fuel Oils. *Langmuir,* 19: 731−736.

Li Y., Wang L-J., Fan H-L., Shangguan J., Wang H., and Mi J (2015). Removal of Sulfur Compounds by a Copper-Based Metal Organic Framework under Ambient Conditions. | *Energy Fuels*, 29: 298−304.

Müller, N. and Rauhut, D (2018). Recent Developments on the Origin and Nature of Reductive Sulfurous Off-Odours in Wine. *Fermentation*, 4: 62

Odigboh, E.U., Moreira, C.A. (2002a). Development of complete cassava harvester, I conceptualization, Agricultural mechanization in Asia, Africa, and Latin America 33(4): 43-49.

Oliveiraa, M. L. M., Mirandaa, A. A. L., Barbosa, C. M. B. M., Cavalcante, C. L., Jr., Azevedoa, D. C. S., Rodriguez-Castellon, E (2009). *Fuels* 88: 1885−1892.

Peralta, D., Chaplais, G., Simon-Masseron, A., Barthelet, K., Pirngruber, G. D. (2012) *Energy Fuels*, 26, 4953−4960

Rauhut, D. (2017). Usage and formation of sulfur compounds. In Biology of Microorganisms on Grapes, in Must and in Wine; König, H., Unden, G., Fröhlich, J., (Eds.) Springer International Publishing AG: Cham, Switzerland,; pp. 255–291

Rauhut, D.; Kürbel, H (1994). The production from H_2S from elemental sulfur residues during fermentation and its influence on the formation of sulfur metabolites causing off-flavours in wine. *Vitic. Enol. Sci.* 49: 27–36.

Rossete A.L.R.M, Bendassolli J.A. and Trivelin P.C.O. (2008). Organic sulfur oxidation to sulfate in soil samples for total sulfur determination by turbidimetry. Sociedade Brasileira de Ciência do Solo Brasil 32 (6): 2547-2553

Shahbaz, M. (2011). Copper toxicity and sulfur metabolism in Chinese cabbage PhD Thesis University of Groningen 131-134 ISBN 9789036750943

Zhou, A., Ma, X., Song, C. (2006). Liquid-Phase Adsorption of Multi-Ring Thiophenic Sulfur Compounds on Carbon Materials with Different Surface Properties *J. Phys. Chem. B* 110: 4699−4707.