

Compatibility of measurement results for the active substance Zineb, determined by CIPAC and ICP-OES methods

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Received November 11, 2016; Revised December 1, 2016

The presented work evaluates the metrological compatibility of the results of the active substances for five batches Zineb, measured by the classical CIPAC25:1993 method in the Accredited Testing Laboratory to Agria S.A., with those measured by a new ICP-OES method. The absolute value of the difference between the measured results for each pair was calculated and was found smaller than twice the standard measurement uncertainty of that difference, which confirmed the compatibility of CIPAC 25 and ICP-OES methods.

The new instrumental ICP-OES method is a faster and "greener" alternative to the classical CIPAC 25 method for determination of the active substance Zineb in biocidal products.

Key words: Zineb, CIPAC, ICP-OES, compatibility

INTRODUCTION

Dithiocarbamates (DTCs) are among the most commonly used classes of organosulfur pesticides. According to the carbon chain DTCs can be divided into the following subsets: DMDs - dimethyl (dithiocarbamates); EBDs - ethylene bis (dithiocarbamates); PBDs - propylene bis (dithiocarbamates) [1]. The object of our study is Zineb - EBD from the so-called "group of Maneb" - Zineb, Maneb, Mancozeb.

Zineb with CAS Number (12122-67-7) has molecular formula $(C_4H_6N_2S_4Zn)_x$, and IUPAC name Zinc ethylene bis (dithiocarbamate). It is a solid, yellowish-white powder with non-characteristic odour.

One of the leading companies in the field of producing, importing and trading with herbicides, fungicides and pesticides is Agria S.A., situated near to Plovdiv, Bulgaria.

Agria S.A. has modern facilities for production, formulation and packaging of plant protection products from the dithiocarbamate group, among them Perozine Marine, which contains Zineb (95% min) as an active ingredient.

Perozine Marine is primarily used as a co-biocide/booster biocide in marine antifouling paints to increase the efficacy of the primary biocide to reduce colonization of biofouling organisms on immersed objects, structures and vessels in the marine environment.

Antifouling paints containing Zineb are applied to the surface of structures to be protected against the build-up of aquatic fouling organisms. This is

achieved via the slow release of the active ingredient over time. These formulations are widely used on the hulls of marine vessels, docks, fishnets and buoys.

Over many years use Zineb has proved to be a very effective partner to the primary biocide in controlling the growth of biofouling organisms. In addition the active ingredient Zineb is considered to be less harmful to the environment than other booster biocides.

In the recent paper [2], Karsaz and Afshar are showing the usefulness of Zineb and Ziram as alternative to the TBT (Tributyltin) which utilization has been stopped since 2003 because of its negative impacts on the marine environment. Comprehensive data about Zineb (product type 21) characteristics and risk assessment of its applications is provided by the European Chemicals Agency (ECHA) in the report published in [3].

For the preparation process of a technical grade pesticide it is very important the active ingredient to be precisely measured and declared.

CIPAC Method 25/TC/M/3 is available to analyze the Zineb content in the Technical Grade of the Active Ingredient (TGAI) [4]. In this paper it will be denoted as CIPAC 25. It is an officially accepted method and is based on the procedure described by D. G. Clarke [5]. The method is set up on the classical titrimetric determination of the carbon disulfide mass fraction produced after thermal degradation of the complex performed by means of an installation called Clarke Apparatus. The testing Laboratory of Agria S.A., which is accredited pursuant to BDS EN ISO/IEC 17025,

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works with this method since many years. It is recommended for the quality control, the accuracy of the results to be proven either by CRM (Certified Reference Materials) or by inter laboratory comparison with different methods of analysis. Moreover the CIPAC 25 measurement procedure uses H₂SO₄, CdSO₄, etc., needs almost an hour to be accomplished and does not belong to the group of environmentally friendly methods. Therefore the replacement of the classical CIPAC 25 method with better, "greener" methods is highly welcomed.

A new instrumental method based on measurements of Zineb bonded sulfur by ICP-OES has been developed by us. The new method was optimized for maximum precision and reliability.

The analytical task is to quantify the active substance – Zineb in manufactured products in the range between 95÷99 % with target uncertainty $u_c < 1\%$ (expanded uncertainty $U < 2\%$, $k=2$). For both CIPAC 25 and ICP-OES methods uncertainty budget was constructed using Kragten [6] spreadsheet approach. The combined uncertainty u_c was calculated according to the EURACHEM / CITAC GUIDE [7]. All experimental data and uncertainty budget constructed for both methods have been reported on the international seminar "Modern methods for chemical analysis and control", organized by Thermo Scientific, ACM2 Ltd and Plovdiv University in Plovdiv 20.05.2015 and have been submitted for publication in another paper. The experiments showed better precision of the instrumental ICP-OES method with higher sample throughput and environmentally friendly characteristics in comparison to the classical one. The combined uncertainty for the active ingredient Zineb measured (96.6 % w/w) was found 0.46% for ICP-OES and 0.82% for CIPAC 25 method respectively.

Due to the fact, that both methods are indirect and use sulfur determination for quantification of Zineb and because in the manufacturing process the product could suffer from some unknown variations, it is needed compatibility of the CIPAC 25 and ICP-OES methods to be checked for different series of technical material. In this work we evaluate the metrological compatibility of both methods. It must be underlined that there are no CRMs with Zineb higher than 95% available on the market. So the comparison by different methods of analysis seems to be the most applicable procedure for quality control.

In the present work the compatibility of the results from CIPAC 25 and ICP-OES analysis has been evaluated according to the method described in [8].

MATERIALS AND METHODS

Apparatuses

CIPAC 25 method

Apparatus for determination of Zineb according to CIPAC 25 (Clarke installation); calibrated balance Mettler AE200; automatic calibrated burette Brand; beaker 600 mL; magnetic stirrer.

ICP-OES method

Thermo ICP-OES iCAP 6300, calibrated balance Mettler AE200; volumetric flask, class AS V =250 mL; US bath, plastic test tubes 50 mL; syringe filter 0.45 μm.

Reagents

CIPAC 25 method

Merck KGaA iodine solution (titrimetric standard), Sigma-Aldrich products: sodium diethyldithiocarbamate trihydrate, sulphuric acid, tetrasodium salt of ethylenediaminetetraacetic acid (EDTA), potassium hydroxide, cadmium sulphate, acetic acid, phenolphthalein indicator solution, starch; deionized water.

ICP-OES method

Sigma-Aldrich sulfur standard for ICP; Merck KGaA ammonia solution; deionized water.

Procedures

CIPAC 25 method

A set of five different batches of Zineb produced in Agria S.A. have been analyzed. 0.3 g of each sample containing Zineb is dissolved in 30% tetrasodium salt of EDTA solution and is decomposed by boiling with 2 mol/L sulphuric acid to ethylenediamine sulphate and carbon disulphide. The latter is passed through a cadmium sulphate (18.5 g in 100 mL distilled water) scrubber to remove hydrogen disulphide, and then into an absorption train containing 2 mol/L methanolic potassium hydroxide to afford potassium methyl xanthate. The produced xanthate, after neutralization with 10% acetic acid, is titrated with 0.05 mol/L iodine standard.

Calculation of Zineb active ingredient (A.I.)

$$A.I. \% = \frac{(A - B) \cdot M \cdot M_m Zb \cdot K}{m \cdot 1000} \cdot 100 \quad (1)$$

A = volume of iodine used for titration of the sample, mL

B = volume of iodine used for titration of the blank, mL

M = molar concentration of iodine, mol/L

M_mZb = molar mass of Zineb, g/mol

m = sample weight, g

K = factor of apparatus

ICP-OES method

The same set of five different batches of Zineb produced in Agria S.A. has been analyzed by ICP-OES. The optimized instrumental conditions are listed in Table 1. External "bracket" calibration

was used. For that purpose two sulfur standard solutions were prepared - 160 and 200 mg/L S in ammonia medium as follows: (i) for 160 mg/L calibrator - 8 g of standard solution of sulfur 1000 mg/L were weighed in a test tube and dissolved to 50 g with 3.75% ammonia (75 mL 25% ammonia to 500 mL with deionized water) and (ii) 10 g standard solution of sulfur 1000 mg/L was dissolved in the same manner for 200 mg/L calibrator.

Sample: 0.2 g Zineb from each batch was dissolved in 250 mL 7.5% ammonia in a volumetric flask. An ultrasonic bath was used for faster dissolution (dilution factor DF = 1250). Second dilution was made just before the instrumental analysis by mixing 25 g of the above sample solution with 25 g of 3.75% ammonia. The final DF = 2500 ensures that in the prepared Zineb samples solution the S concentration will lie between the bracket standards.

For determination of unbonded sulfur, water extracts have been developed as follows: 0.5 g of each batch Zineb was suspended in 50 g deionized water. The sample solution was filtered through syringe filter 0.45 µm. Second dilution was made just before the instrumental analysis by mixing 25 g of the above sample solution with 25 g of 7.5% ammonia.

Table 1. Instrumental parameters of the ICP-OES determination of sulfur

Parameter	Value
Radiofrequency power	1250 W
Plasma gas flow rate	15 L min ⁻¹
Auxiliary gas flow rate	0.5 L min ⁻¹
Nebulizing/carrier gas flow rate	0.7 L min ⁻¹
Peak processing	3 pixels per peak
Background correction	2 sides one pixel
Number of replicates	4
Replicate read time	10 s
Nebulizer type	OneNeb Flow Blurring® nebulizer
Sample flow rate	1.2 mL min ⁻¹
Spray chamber	Single-pass cyclonic chamber
Viewing mode	Axial
Spectral lines for sulfur	182.624 nm

Calculation of Zineb active ingredient (A.I.) after ICP-OES determination of sulfur

$$A.I. \% = \frac{C_z \cdot V_{pr} \cdot m_{2pr} \cdot M_m Zb.}{m_{pr} \cdot m_{1pr} \cdot 4 \cdot A_m S} \cdot 100 \quad (2)$$

C_z= content of bonded in the Zineb sulfur (measured by ICP-OES), mg/ml

V_{pr} = initial volume for sample dissolution, ml

m_{1pr}= amount of sample solution taken, g
m_{2pr} = final sample weight (for second dilution),g

M_mZb = molar mass of Zineb, g/mol

A_mS = atomic weight of sulfur, g/mol

m_{pr} = sample weight, mg

ICP-OES determination of sulfur after "bracket" calibration

$$C_z \frac{mg}{l} = \frac{C_1 \left(I_2 - \left(I_z - \frac{I_0}{F} \right) \right) + C_2 \left(\left(I_z - \frac{I_0}{F} \right) - I_1 \right)}{I_2 - I_1} \quad (3)$$

I_z = intensity of the sample Zineb, cps

I₀ = intensity of the extracted sample Zineb, cps

I₁ = intensity of the low standard of S, cps

I₂ = intensity of the high standard of S, cps

F = ratio between concentrations of Zineb sample and the extracted one

C₁= concentration of the low standard, mg/mL

C₂= concentration of the high standard, mg/mL

RESULTS AND DISCUSSION

Despite the fact that the manufacturing process of technical Zineb (near 95%) is strictly controlled the final product differs in the active substance content from 95 till 99%. Fit for purpose analysis has to be performed to justify the particular content of the active ingredient. Therefore representative samples from five batches of Zineb, manufactured in different days in Agria S.A. have been collected. For each batch the active substance Zineb was determined by the CIPAC 25 method in the Testing Laboratory of Agria S.A. and by the ICP-OES method in the laboratory of the University of Plovdiv, Department of Analytical Chemistry and Computer Chemistry. Results obtained from both methods are listed on columns (2) and (3) in Table 2. No reference material Zineb was available, hence the reliability of the tests could be concluded if the results from both methods are compatible.

One commonly used approach described in the textbooks [9] for comparing analytical methods is the use of regression lines. In this approach one axis of a regression graph is used for the results obtained by the classical method, and the other axis for the results obtained by applying the new or comparative method to the same samples. It is clear that if each sample yields an identical result with both analytical methods, the regression line will have a zero intercept "a", with a slope "b" and a correlation coefficient "r" - equal to 1. In the current case however the commented above regression approach is inapplicable and can give unreliable estimations.

Working with the sets of data from Table 2 and using the line regression approach (CIPAC25 versus ICP-OES), the calculated parameters are $b = 1.65$; $a = 62.5$ and $r = 0.985$, which are quite far from the ideal case. The reason is that all five

samples tested, contain Zineb in pretty close concentration to the centroid – 96.6 %, and due to the uncertainty attributed to the results it seems we do evaluation of regression with very close to one point of concentration, which is a nonsense.

Table 2. CIPAC and ICP-OES results and their estimators of compatibility (see in the text) for determination of the active substance Zineb in percent (%)

No batch	CIPAC 25 x_c	ICP-OES			u_c	u_i	u_d	ku_d
		x_i	$ x_i - x_c $					
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	
1	95.51	95.05	0.46	0.78	0.44	0.90	1.79	
2	95.71	95.40	0.31	0.78	0.44	0.90	1.80	
3	96.66	97.35	0.69	0.79	0.45	0.91	1.82	
4	96.73	97.44	0.71	0.79	0.45	0.91	1.82	
5	97.63	98.40	0.77	0.80	0.45	0.92	1.84	

Therefore another approach using the model given in [8] was selected as a more reliable estimator of the compatibility of both methods for Zineb quantification. The metrological compatibility of measuring results is defined in [VIM3 2.47] [10] as: "property of a set of measurement results for a specified measurand, such that the absolute value of the difference for any pair of measured quantity values from two different measurement results is smaller than some chosen multiple of the standard measurement uncertainty of that difference". In our case and according to [8] the compatibility could be proved if the absolute value of the difference $|x_i - x_c|$ for each pair of results (ICP-OES – CIPAC25) is smaller than the combined uncertainty of the difference u_d multiplied by the coverage factor $k=2$.

Hence for the data in Table 2 the difference d for each pair (x_i – for ICP-OES method and x_c - for CIPAC 25 method) was found and the absolute value is given on column (4). The combined uncertainty u_d of the difference for each pair of measurement results was calculated according to the propagation law using the equation 4:

$$u_d = \sqrt{u_i^2 + u_c^2} \quad (4)$$

The u_c and u_i from columns (5) and (6) on Table 2 are the combined uncertainties estimated for CIPAC 25 and ICP-OES measurements of Zineb respectively.

The obtained u_d are listed in column (7)

As one can see, all the five values in column (4) are smaller than those in column (8) which is the condition to claim that the results are compatible:

$$|x_i - x_c| < ku_d \quad (5)$$

samples tested, contain Zineb in pretty close concentration to the centroid – 96.6 %, and due to the uncertainty attributed to the results it seems we do evaluation of regression with very close to one point of concentration, which is a nonsense.

Moreover all the five values in column (4) are smaller than those in column (7) which is even more significant proof.

Figure 1 was constructed with the same data from Table 2 but averaged points (from CIPAC 25 and ICP-OES) have been added for each batch sample tested with dotted line for CIPAC 25 and solid line for ICP-OES. It is important to emphasize that lines are crossed and with a different distance between them. All this is an evidence for the existence of random effects in the measurement shifts rather than a systematical one.

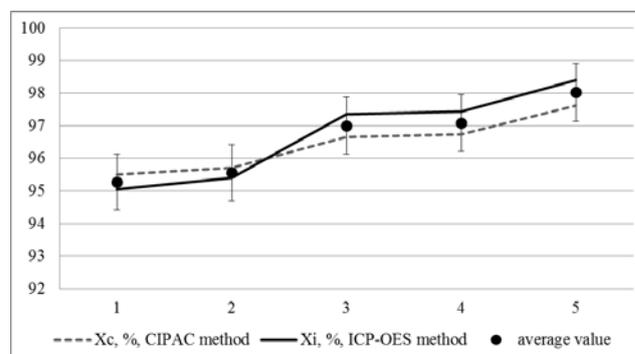


Fig. 1 Plotted results for the active substance zineb (the error bars shows the target uncertainty)

CONCLUSION

The new instrumental ICP-OES method is a faster and "greener" alternative to the classical CIPAC 25 method for determination of the active substance Zineb in biocidal products. The metrological compatibility between the new ICP-OES method and CIPAC method is proved for measuring concentrations near 96.6 % with fit for purpose accuracy. The absolute value of the difference between measured results for each

measurement pair is smaller than twice the standard measurement uncertainty of that difference, and confirms the compatibility of the methods.

ICP-OES method could be recommended for wider use.

Acknowledgements: *The current study was supported by the Fund for Scientific Research of the University of Plovdiv project NI 15-HF 001.*

REFERENCES

1. G. Crnogorac and W. Schwack, *TrAC Trends in Analytical Chemistry*, **28**(1) 40-50, (2009).
2. A. Karsaz, A. Afshar, *J. Mater. Environ.*, **7**(4) 1436-1444, (2016).
3. Regulation (EU) n0528/2012, Zineb Product-Type 21 (Anti-fouling products), S.C.o.B. Products, Editor. (2013).
4. W. Dobrat, A. Martijn, *CIPAC. Vol. Handbook E*, (1993).
5. D. Clarke, et al., *Analytical Chemistry*, **23**(12) 1842-1846, (1951).
6. J. Kragten, *Analyst*, **119**(10) 2161-2165, (1994).
7. Eurachem/CITAC QUAM Guide CG 4 (Third Edition), (2012).
8. T. Linsinger, *European Reference Materials, Application note one*, (2010).
9. J. Miller, J. Miller, *Statistics and Chemometrics for Analytical Chemistry, Fifth edition*, p. 126, (2005).
10. V. Barwick, E. Pichard, *Eurachem Guide: TAM-Introduction to VIM 3*, (2011).

СЪВМЕСТИМОСТ НА РЕЗУЛТАТИТЕ ОТ АНАЛИЗ НА АКТИВНАТА СУБСТАНЦИЯ ЦИНЕБ, ОПРЕДЕЛЕНА ЧРЕЗ СІРАС И ІСР-ОЕС МЕТОДИ

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Постъпила на 11 ноември 2016 г.; приета на 1 декември 2016 г.

(Резюме)

Представената работа оценява метрологичната съвместимост на резултатите от определянето на активната субстанция в пет партии Цинеб произведен в Агрив АД, измерени чрез класически СІРАС 25: 1993 метод в акредитираната лаборатория към Агрив АД, с тези, измерени чрез новосъздаден ІСР-ОЕС метод. Абсолютната стойност на разликата между измерените резултати за всяка двойка е по-малка от два пъти стандартната неопределеност при измерване на тази разлика, което потвърждава съвместимостта на СІРАС 25 и ІСР-ОЕС методите.

Новосъздаденият ІСР-ОЕС инструментален метод е по-бърза и по-„зелена“ алтернатива на класическия СІРАС 25 метод за определяне на активната субстанция Цинеб в биоцидни продукти.

Ключови думи: *Цинеб, СІРАС, ІСР-ОЕС, метрологична съвместимост*