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Publisher *Taylor & Francis*

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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article Alarcón, P. , Alonso, E. , Benito, Y. , De La Fuente, P. and Vergara, A.(1989) 'Comparative Study about Cd, Cr, Fe and Mn Determination in Natural and Wastewater by AA and DCP Techniques', *International Journal of Environmental Analytical Chemistry*, 37: 2, 75 – 82

To link to this Article: DOI: 10.1080/03067318908026887

URL: <http://dx.doi.org/10.1080/03067318908026887>

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COMPARATIVE STUDY ABOUT Cd, Cr, Fe AND Mn DETERMINATION IN NATURAL AND WASTEWATER BY AA AND DCP TECHNIQUES*

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Cd, Cr, Fe and Mn were analyzed by DCP and GFAAS in natural and wastewater spiked samples. A statistic study was realized to probe that both techniques reach comparable results in the intervals: 5–50 $\mu\text{g L}^{-1}$ for Cd, 10–100 $\mu\text{g L}^{-1}$ for Cr, 50–500 $\mu\text{g L}^{-1}$ for Fe, and 10–100 $\mu\text{g L}^{-1}$ for Mn.

The test shows that the flameless AA technique sensitivity is higher than DCPs, but the last one achieves the legal Spanish allowable limits. According to the amount and kind of samples that are analyzed in the IGME laboratories it can be deduced that DCP being simultaneous technique, one gets more sample throughput in the mentioned intervals.

KEY WORDS: Micropollutants, flameless atomic absorption spectroscopy, plasma atomic emission spectroscopy, groundwater, industrial waste waters.

1. INTRODUCTION

In the last years the pollution of continental and marine water has been an important theme in the world actuality. Modern analytical techniques have shown the general environmental distribution of elements known as "Heavy Metals".

Among this group of elements, cadmium is one of the most dangerous for its bioaccumulation capacity.¹ Its maximum allowable limit (MAL) in Spanish legislation is 10 $\mu\text{g L}^{-1}$ for bottled water. This is the second lowest MAL, the first is 1 $\mu\text{g L}^{-1}$ for mercury.² The toxicity of chromium depends on its molecular type and oxidation state,³ its MAL is 50 $\mu\text{g L}^{-1}$. Manganese has the same MAL as chromium, 50 $\mu\text{g L}^{-1}$, and iron with 100 $\mu\text{g L}^{-1}$ has the highest MAL.²

Different water samples are analyzed during the IGME groundwater resources policy program. The first objective of this program is checking the potability

*Presented at the 18th International Symposium on Environmental and Analytical Chemistry, Barcelona, 5–8 September 1988.

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according to Spanish legislation.² Industrial wastewater discharges are also monitored in order to inspect their environmental pollution capacity.

Analysis of these elements are made with the Grafite Furnace Atomic Absorption Spectrophotometry (GFAAS) technique. Cadmium and chromium do not show any trouble, but this is not the case for iron and manganese. These elements show near its maximum sensitivity lines other ones (Fe 248.8 and Mn 279.8 nm). In this circumstance, the work with narrow bandwidth (0.3 nm) is mandatory, but makes background correction more difficult. Also, iron and manganese determination shows troubles associated with matrix interferences.

DCP technique shows practically no matrix interferences and the possibility of multi-element determinations, although with minor sensitivity performances.

The present work tries to compare both techniques getting legal MALs, and decreasing analysis time.

2. EXPERIMENTAL

2.1 General

Reagent HNO₃ Suprapur (Merck, Darmstadt, FRG). Cd, Cr, Fe and Mn certificated standard of 1000 mg L⁻¹ (Fisher Scientific Co., Fair Lawn, NJ, USA).

Water samples Groundwater: Conductivity 400–700 μs, oxidability (MnO₄⁻) 0.5–2.0 mg O₂ L⁻¹. Industrial wastewater: Conductivity 3400–4200 μs, oxidability (MnO₄⁻) 2.0–14.0 mg O₂ L⁻¹. Cd, Cr, Mn and Fe concentrations are lower than the tenth part of MAL in groundwater and industrial wastewater.

Water spiking Five 200 mL groundwater samples and another of wastewater are spiked with element concentrations in the rank Cd (5–50 μg L⁻¹), Cr (10–100 μg L⁻¹), Fe (50–500 μg L⁻¹) and Mn (10–100 μg L⁻¹). All the spiked samples are preserved with 0.5% HNO₃ 40 g L⁻¹ lithium concentration and 0.1 N HCl are added before DCP analysis.

2.2 AA Spectrophotometry

Instrumentation Spectrophotometer IL 951 (Instrumentation Laboratory, Wilmington, MA, USA). Atomizer IL 555 with pirolitic coated graphite cassettes. Automatic injector FASTAC IL 254.

Experimental methods The spectrophotometer are calibrated with five element standard solutions series. These solutions are made up with the 1000 mg L⁻¹ standard. The element selected wavelengths are shown in Table 1.

All the laboratory glassware have been washed and maintained in 10% (v/v) HNO₃ solution.

Table 1 GFAAS and DCP wavelengths

Element	GFAAS			DCP		
	nm	BW nm	BC	nm	Order no.	Slit nm
Cd	228.8	1.0	No	228.8	98	0.1
Cr	357.9	1.0	No	425.4	53	0.1
Fe	248.3	0.3	Yes	259.9	87	0.1
Mn	279.5	0.3	Yes	403.0	56	0.1

BW, bandwidth; BC, background corrector (D₂).

2.3 DCP Spectrophotometry

Instrumentation The plasma spectrophotometer used in this work, was a d.c. plasma atomic emission, model Spectraspan IIIB (Spectrametrics, Inc., USA), equipped with three electrodes.

The argon plasma is formed between two anodes and a tungsten cathode in an inverted Y configuration.

The instrument was equipped with two cassettes of preselected lines for the multi-element analysis with 20 exit slits.⁴

The spectrometer had two background correctors (DBC-33) and an autosampler.⁴

Analytical wavelength selections Elements selected for the present investigation were Cd, Cr, Fe and Mn. Analytical wavelengths were selected on the maximum sensitivity and minimum spectral interference, and using the two multi-element cassettes.⁵

Analytical wavelengths and exit slit widths are listed in Table 1.

Adjustment and calibration Argon flow, argon pressure (nebulizer: 30 psi, electrode sleeves: 50 psi) and photomultiplier gain, were adjusted to maximize the emission intensity of the interest line with reasonable stability and then, held constant. The same with the optimum plasma position and cassette alignment, these were established by using the emission from a multi-element standard.⁶

Calibration of the instrument is performed with high and low standards (the high standard is a multi-element standard with the same concentration for all elements: 200 $\mu\text{g L}^{-1}$) and the low standard is the blank prepared in the same ionic buffer as the samples.⁶

The buffer was prepared with a 40 g L^{-1} lithium concentration and 0.1 N HCl final acid concentration.

After calibration, the standard and the blank solutions were each reanalyzed after eight measures to verify the stability.

There is no coincidence of emission lines, neither overlap of analytical coefficients. The determination does not need an internal standard because there are no physical interferences.

Table 2 Cadmium determination in spiked ground-water and wastewater samples

Sample	Groundwater		Wastewater	
	GFAAS	DCP	GFAAS	DCP
1	0.049	0.049	0.050	0.051
2	0.024	0.032	0.021	0.029
3	0.010	0.014	0.011	0.011
4	0.006	0.007	0.005	0.005
5	0.004	0.004	0.003	0.004

GFAAS and DCP determination in mg L^{-1} . Arithmetic mean ($n=2$).

Table 3 Chromium determination in spiked ground-water and wastewater samples

Sample	Groundwater		Wastewater	
	GFAAS	DCP	GFAAS	DCP
1	0.100	0.102	0.110	0.101
2	0.070	0.071	0.075	0.078
3	0.045	0.047	0.050	0.048
4	0.035	0.024	0.025	0.024
5	0.012	0.012	0.012	0.017

GFAAS and DCP determination in mg L^{-1} . Arithmetic mean ($n=2$).

3. RESULTS AND DISCUSSION

A method for the determination of a particular analyte can be tested by applying it to a series of samples already studied by the use of another reputable procedure. In order to find out if the DCP method can be used by IGME, this is tested with the GFAAS method and two water samples series are spiked (2.1). These water samples belong to the kind of samples most frequently analyzed by IGME: groundwater and wastewater.

In cases where an analysis is repeated several times over a very limited concentration range, the comparison can be made by using different statistical tests (Fisher test;⁷ Paired t -test⁸). Such procedures will not be appropriate over large concentration ranges. When two methods have to be compared at different analyte concentrations, the use of regression analysis is a better procedure. One variable is used for the results obtained by applying the comparison method to the same samples.

If each sample yields an identical result with both analytical methods, the regression line will have a zero intercept, and a slope and a correlation coefficient of 1. Deviations from this ideal situation can be tested by determining the confidence limits for the slope and intercept.⁸

Results obtained for Cd, Cr, Fe and Mn spiked samples are shown in Tables 2–5, these ones are roughly the same for both methods in each kind of sample. These results are plotted on regression lines (Figures 1–4) with the GFAAS results assigned to the x-axis and the DCP ones to the y-axis.

Table 4 Iron determination in spiked groundwater and wastewater samples

Sample	Groundwater		Wastewater	
	GFAAS	DCP	GFAAS	DCP
1	0.505	0.442	0.490	0.476
2	0.230	0.209	0.250	0.242
3	0.090	0.100	0.120	0.113
4	0.070	0.066	0.450	0.468
5	0.025	0.023	0.155	0.158

GFAAS and DCP determination in mg L^{-1} . Arithmetic mean ($n=2$).

Table 5 Manganese determination in spiked groundwater and wastewater samples

Sample	Groundwater		Wastewater	
	GFAAS	DCP	GFAAS	DCP
1	0.102	0.103	0.097	0.096
2	0.067	0.068	0.066	0.067
3	0.067	0.062	0.050	0.047
4	0.027	0.026	0.025	0.023
5	0.008	0.008	0.010	0.011

GFAAS and DCP determination in mg L^{-1} . Arithmetic mean ($n=2$).

Table 6 Regression lines of DCP versus GFAAS results

Element	Slope	Intercept	Correlation coefficient
Cd	1.013 ± 0.047	2.06 ± 1.16	0.9845
Cr	0.970 ± 0.038	0.59 ± 2.37	0.9888
Fe	0.945 ± 0.028	4.26 ± 8.25	0.9934
Mn	1.000 ± 0.016	-0.81 ± 0.96	0.9982

Intercept (ng mL^{-1}) and slope with the 95% confidence limits.

Values for the slope (B), the intercept (A), the correlation coefficient (r) and the confidence limits for slope and intercept are calculated with usual methods.⁸ These ones are presented in Table 6.

From these values it is clear that slope and intercept do not differ significantly from 1 and zero respectively, and thus there is no evidence for systematic differences between the two sets of results for Cr and Mn.

Cadmium shows the intercept higher than zero, DCP method yields a result higher than GFAAS by an amount of 0.002 mg L^{-1} . This might show a wrongly calculated background signal, probably an element loss in the pyrolysis stage of electrothermal heating in GFAAS.

Iron shows the slope lower than 1 indicating a systematic error, probably due to

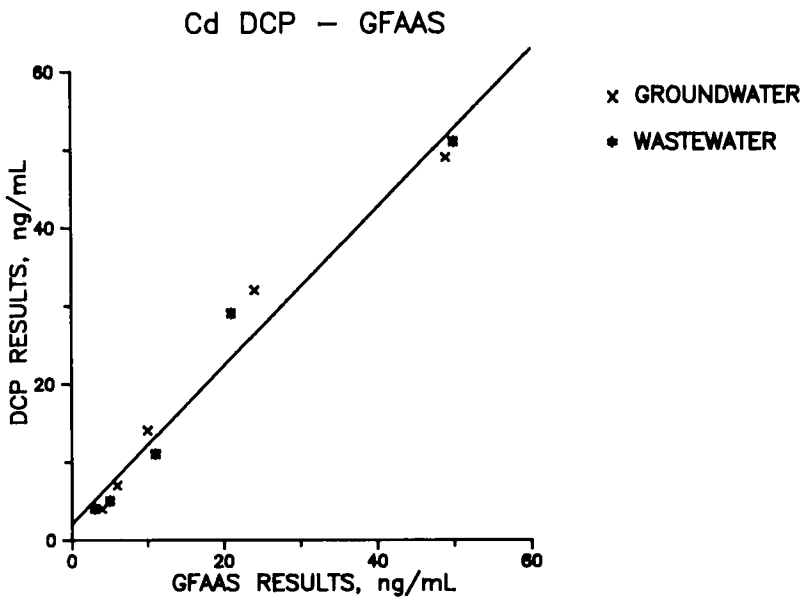


Figure 1 Cadmium regression line of DCP versus GFAAS results.

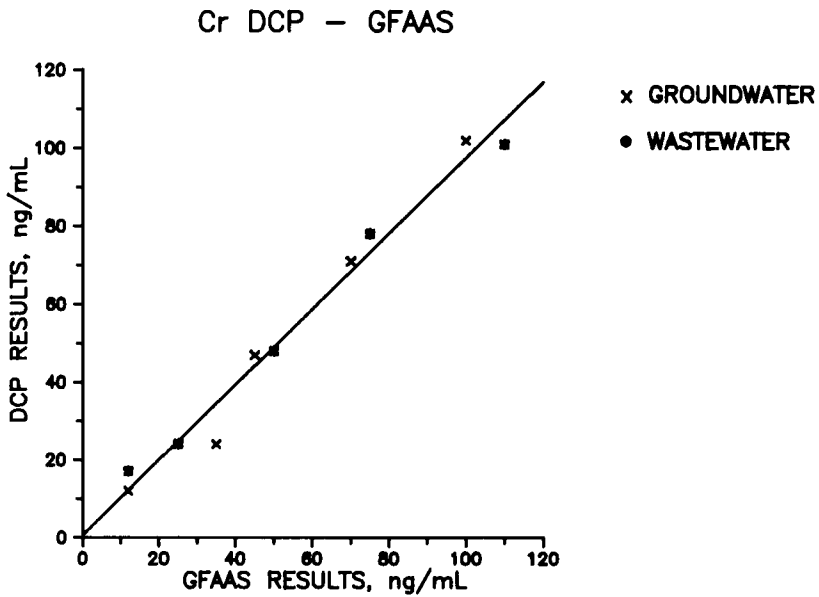


Figure 2 Chromium regression line of DCP versus GFAAS results.

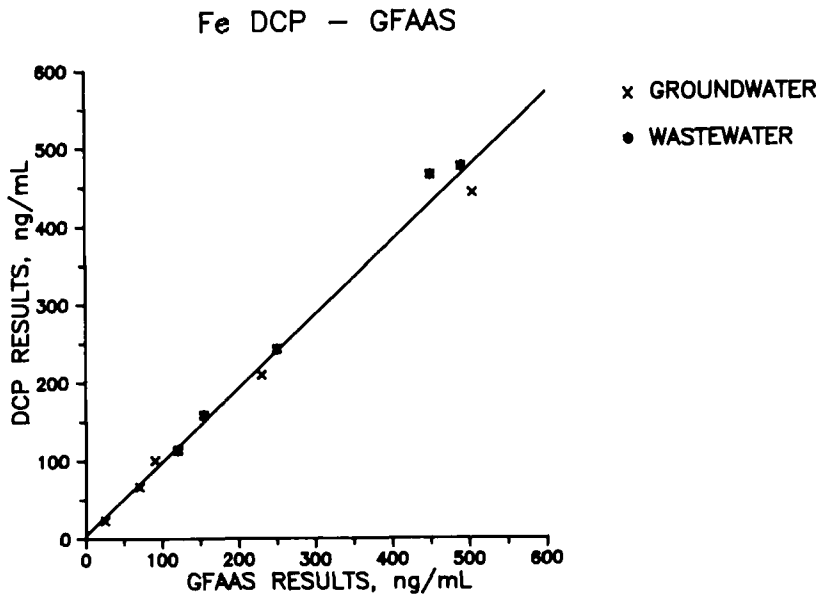


Figure 3 Iron regression line of DCP versus GFAAS results.

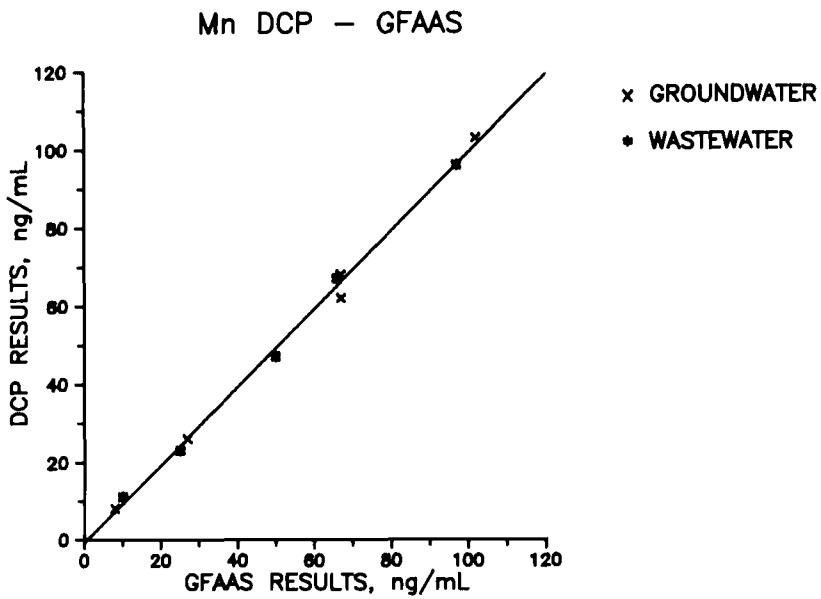


Figure 4 Manganese regression line of DCP versus GFAAS results.

non-uniform distribution of experimental points. Other experiments have still to be conducted.

With all elements DCP reach the MAL, under GFAAS experimental conditions these met difficulty. The reasons are troubles associated with signal saturation, proving the better sensitivity of GFAAS.

Acknowledgement

The authors wish to thank Mr S. Del Barrio for his contribution in the realization of DCP determinations.

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