Influence of water sample storage protocols in chemiluminescence detection of trace elements

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Abstract

This paper shows the influence of different sample storage protocols, on the chemiluminescence signal of some metal ions. The storage protocols studied were: acid addition (HCl or HNO3) and no reagent addition to filtered and refrigerated (T_/4 8C) samples. Light emission was produced for the chemiluminescence reaction between luminol and hydrogen peroxide in buffer carbonate conditions (pH 10.8) catalysed by Cr(III), Co(II) and Cu(II). Batch and/or flow modes in different conditions were tested. Fe(II), Fe(III), Ni(II) and Mn(II) did not give chemiluminescence in the studied conditions. A parallel study of sensitivity and selectivity was performed. Then the presence or absence of the masking agent EDTA, added to samples or used in the carrier stream, is assayed. If the samples are acidified with

HNO3, a previous neutralisation is needed using batch mode. The determination of Cr(III) is independent of storage protocol by flow injection (FI) method; however, the determination of Co(II) or Cu(II) or total determination of three metals requires the conditioning of standards. Detection limits achieved are ranged between 0.5 and 2 mg l_1. For batch mode, detection limits are better for unacidified samples and worse for carbonate-neutralised samples. The influence of storage protocols was validated using standard metal mixtures and calibration solutions. The use of standard reference material (SRM# 1640) (Trace elements in natural water) corroborates the previous statements and validates the accuracy of the different approaches underlined. This paper demonstrates that it is possible to determine Cr(III) selectively in natural waters.

Keywords: Chemiluminescence; Metal determination; Storage protocols; Luminol_/hydrogen peroxide reaction

1. Introduction

The preservation of samples is an interesting analytical problem because complete stability for every constituent can never be achieved. After sample collection, preservation procedures only retard chemical and biological changes [1]. Adsorption on the walls of the vessels will take place for samples stored unacidified and unfrozen. Samples may be stored unacidified but frozen in order to preserve the original distribution of the species [2]. Independent of storage temperature, most authors recommend acidification immediately after sampling if metal ions want to be assayed. Immediate analysis is always recommended for metal determination in water samples. Short storage of filtered sample at low temperature (4 8C) is also used. In these cases, the measurement is realised without further sample conditioning step. The analysis of bottled water is also performed without this step. The most common storage method for metal determination in water samples is to add an acid as HCl up to pH around 2_ 3. The previously filtered samples are stored in plastic acid washed containers at 4 8C. The maximum storage recommended and regulated is 6 months. The procedure employed for long-term storage uses the addition of HNO3 acid. The samples are filtered, acidified and stored at 4 8C. Polyethylene bottles can be sealed in aluminised plastic bags. The storage period can last even 2_ 3 years. Standard reference materials are prepared according to this protocol.

Determination of trace elements in environmental water samples requires analytical techniques with high sensitivity and selectivity. Unielemental techniques like atomic absorption

spectrometry (AAS) (flame or electrothermal) or multielemental techniques like atomic emission spectrometry (ICP) alone or coupled with mass spectrometry (ICP_ MS) have been used for the determination of metal ions.

Chemiluminescence from reactions that usually produces transient emissions is also an attractive and alternative method for determining some trace metal ions. Chemiluminescence provides sensitivity and selectivity and coupled to flow injection (FI) fast and reproducible sample injection and mixing of the reagents. These factors, together with low cost compared with AAS and ICP techniques, simplicity and the possibility to realise easily in situ analysis make a chemiluminescence determination or its combination with FI extremely attractive.

Table 1 shows a selection of flow injection_ chemiluminescence determinations of metal ions in aqueous samples described in the literature [3_ 23]. The reaction more often used is the oxidation of luminol by hydrogen peroxide in alkaline solution catalysed by some metal ions, producing chemiluminescence emission at l_ 425 nm. A preconcentration step is necessary for quantifying Fe(II), Fe(III), Mn(II) and Cu(II). The most common method is ion exchange chromatography. It is important to emphasise the critical effect of the eluent and pH. The majority of methods determine Cr(III) without preconcentration. Several reagents have been used for masking interferences, e.g. for Mn(II), Co(II) and Cr(III), 8-quinolinol, sodium citrate and EDTA have been used, respectively. Moreover in some procedures, standards and samples are conditioned with H3PO4 to mask the interfering ions. As it can be seen in Table 1, the experimental conditions influence the figures of merit of the procedures. The aim of this paper was to study the direct chemiluminescence signal for Cr(III), Co(II), Fe(II), Fe(III), Ni(II) and Mn(II) as function of sample storage procedure. The chemiluminescence emission is produced by luminol_ H2O2 reaction catalysed by metal ions. In the literature considerations about the influence of the sample storage conditions on chemiluminescence signal are not reported. According to previous considerations, no acidified samples and acidified samples with hydrochloric or nitric acids were tested in this paper. The alternatives for determining samples stored in acidic conditions were tested in batch and FI modes. Also, the employment of a masking agent in reagent composition or as sample treatment step has been compared in order to improve the selectivity for chromium determination. Finally, the standard reference material (SRM# 1640) was used for testing accuracy and establishing conclusions.

2. Experimental

2.1. Apparatus and reagents

Hitachi F4500 (Tokyo, Japan) and Jasco FP- 750 (Tokyo, Japan) fluorescence spectrophotometers were used for measuring. The light emission was monitored at 425 nm. The following analytical grade reagents were used: chromium(III) potassium sulphate 12-hydrate (Merk, Germany), cobalt(II) nitrate 6-hydrate (Panreac, Spain), copper(II) sulphate 5-hydrate (Merk), ammonium iron(II) sulphate 6- hydrate (Panreac), ammonium iron(III) sulphate 12-hydrate (Panreac), nickel(II) nitrate 6-hydrate (Merk) and manganese sulphate hydrate (Panreac). Other reagents were hydrogen peroxide (Panreac), EDTA (Probus, Spain), luminol (Fluka, Switzerland), sodium carbonate (Merk), potassium hydroxide (Probus), hydrochloric acid 36% (Merk) and nitric acid (Merk). The solutions were prepared in water (nanopure, Sybron, Barnstead, Spain). For FI assembly, a Gilson Miniplus peristaltic pump was used to drive the reagent_ sample mixture through the flow cell. The loop employed has a 200 ml internal volume. Tygon tubing (i.d._ 0.8 mm) was used with the peristaltic pump. The flow cell was a spiral cell, consisted of laboratorymade coiled transparent poly(tetrafluoroethylene) tubes measuring 50 cm in length and with i.d._ 0.8 mm. The dimensions of the cell were 1 cm of internal diameter and 3 cm of external diameter.

2.2. Procedures

A cleaning procedure was applied to glassware, containers and other glass or plastic materials. The first step was rinsing with nanopure water, later 10% HCl bath overnight and rinsing with nanopure water again. The concentration of Cr(III), Co(II), Cu(II), Fe(II), Fe(III), Ni(II) and Mn(II) standard solutions was 1000 mg l_1.Working solutions of metal ions were prepared daily. The measurement assemblies are described in Ref. [23].

2.2.1. Batch procedure

The reagent stock solutions were 1.2_ 10_3 mol l_1 luminol in 0.3 mol l_1 CO3 2_/HCO3 _ (pH 10.8), 0.1 mol l_1 H2O2, 0.01 mol l_1 EDTA in 0.02 mol l_1 KOH or in 0.3 mol l_1 CO3 2 _/ HCO3 _ (pH 10.8). Different reaction solutions were prepared directly into a quartz cell. The injection of the sample (200 ml) was carried out with a Hamilton digital syringe throughout a septum and mixed with a magnetic agitator. The FP-750 Jasco spectrophotometer was used for monitoring.

2.2.2. FI procedure

Luminol solution of 1.2_ 10_3 mol l_1 in 0.3 mol l_1 CO3 2_/HCO3 _ (pH 10.8) and 0.1 mol l_1 H2O2 were first mixed in the flow system and then mixed with the sample carrier. Different carrier compositions were studied: 0.3 mol l_1 CO3 2_/ HCO3 _ (pH 10.8), 1_ 10_2 and 5_ 10_3 mol l_1 EDTA in 0.02 mol l_1 KOH, 1_ 10_2 and 5_ 10_3 mol l_1 EDTA in 0.3 mol l_1 CO3 2_/HCO3 _ (pH 10.8). In all cases, the injection volume was 200 ml. The Hitachi F4500 spectrophotometer was used for measuring. Different conditioning procedures were studied: without conditioning, addition of 5_ 10_3 mol l_1 HCl and addition of 0.5 mol l_1 HNO3. In some cases, a masking agent was added 1_ 10_2 mol l_1 or 5_ 10_3 mol l_1 EDTA.

2.2.3. Validation procedure

Standard mixtures of different metal ions were prepared. The bicomponent and tricomponent solutions are described in Table 2. Additionally, calibration standard solutions were prepared in different conditions (see Table 3). A standard material reference was also analysed. SRM# 1640 (NIST, USA) is composed of natural fresh water collected from Cleark Creek, CO, which had been filtrated and stabilised with nitric acid.

3. Results and discussion

3.1. Chemiluminescence signal of unacidified samples

The chemiluminescence signal of standards prepared in ultrapure water was studied first. Specific laws fix upper levels of these metals in water of 200 mg l_1 for Fe, 20 mg l_1 for Ni, 2 mg l_1 for Cu and 50 mg l_1 for Cr (European directive 98/83/ EC). The trace elements composition of fresh water can be described by the SRM# 1640 contents (Table 4). Chemiluminescence coupled to FI was previously studied. Ni(II) and Mn(II) signals were similar to blank signal. The chemiluminescence emission of Fe(II) and Fe(III) was only quantifiable for concentrations superior to upper levels legislated. It will be necessary to use a preconcentration step to apply the method for determining these metals yet. Cr(III), Co(II) and Cu(II) provided enough signals to their direct quantification. Some authors have proposed the use of EDTA in order to mask some interferences, especially for the determination of Cr(III). EDTA was added to the carrier solution or sample solution, then the metal_ EDTA complex was formed in the FI system or before the FI system, respectively.

The signal (S) can be described as function of metal concentration (cM): S_acb M; where a and b are constants. A straight line was obtained for double logarithmic calibration plot: log S_ log a_ b log cM. Table 5 shows the calibration parameters of double logarithmic or potential regression for different experimental conditions. The peak height was used as analytical signal. The 3_ 15 mg l_1 concentration interval for Cr(III) provided a linear calibration model. The working linear interval for Co was 2_ 8 mg l_1 and for Cu the linear interval was up to 20 mg l_1. The detection limits calculated for a signal-to-noise ratio of 3 were 0.5_ 2 mg l_1. These values are similar to those provided by electrothermal atomic absorption for these trace elements [24]. To increase the selectivity of Cr(III) determination, EDTA was added to sample solution or carrier solution, then the metal_ EDTA complex was formed before or in the FI system, respectively. Co(II) sensitivity decreased drastically in the presence of EDTA and the Cu(II) signal disappeared. The sensitivity of Cr(III) decreased when EDTA 0.01 mol l_1 was added in carrier, as it can be seen in Table 5. The addition of the masking agent to samples provided worse sensitivities similar to that observed by the use of EDTA 0.01 mol l_1 in carrier stream. For batch procedure and in the presence of 3_ 10_3 mol l_1 EDTA, the calibration curves are shown in Table 6. The selectivity for Cr was three times higher than for Co as it can be seen in this table. The batch measurements provided the following equation:

(0.079 0.05)_ (0.309 0.02)cM (R2_ 0.997, syx_ 0.07). Comparing both calibration slopes, the loss of sensitivity of the FI procedure is about 55%.

3.2. Chemiluminescence signal of samples stored in HCl

Calibration in acidic conditions was evaluated with the addition of 5_ 10_3 mol l_1 HCl. Without EDTA, the sensitivities obtained for Cr(III), Co(II) and Cu(II) were similar to those obtained in acidified conditions. The presence of EDTA in carrier solution or sample, as masking agent, was also studied. Table 7 shows the calibration parameters for the different calibration models and experimental conditions. Sensitivity values achieved were similar to previous conditions. The detection limits achieved without EDTA for Cr(III), Co(II) and Cu(II) were similar to those indicated above. Similar detection limit was obtained for Cr(III) in presence of EDTA, Cu(II) was not detected and Co(II) increases its detection limit up to around 50 mg l_1. The sensitivities obtained for Cr and Co by the batch mode were 0.898 and 0.35, respectively. These values were similar to those reported in Table 6 for unacidified samples.

3.3. Chemiluminescence signal of samples stored in HNO3

Chemiluminescence emission was studied in drastic acidic conditions (0.5 mol l_1 HNO3). Table 8 shows the calibration parameters in conditions without EDTA addition obtained by FI procedure. The sensitivities achieved for the three trace elements, Cr(III), Co(II) and Cu(II), were worse than those obtained in the two previously studied conditions without EDTA addition. However, the slope value for Cr(III) was similar to that obtained in unacidified or HCl acidified standards when 0.01 mol l_1 EDTA was used. The detection limits achieved calculated for a signal-to-noise ratio of 3, are 3, 3.5 and 10 mg l_1 for Cr, Co and Cu, respectively. For batch procedure, neutralisation of sample was required. The best results were obtained using 0.2272 mol l_1 Na2CO3 considering a dilution 7/ 10 for samples. The Cr and Co chemiluminescence signals are given in Fig. 1. The calibration curves were (_ 0.49 0.2)_ (0.389 0.01)cCr (R2_ 0.99, syx_ 1.5) and (_ 0.29 0.2)_ (0.549 0.01)cCo (R2_ 0.99, syx_ 0.1).

3.4. Applicability

Fig. 2 shows the signal obtained for the different studied conditions using the FI method. The chemiluminescence signal for each metal was function on sample storage procedure and the presence of masking agent, although the influence was low for Cr. Specificity of chromium determination can be achieved adding EDTA. No neutralisation was needed to process the samples stored in the different options tested when the FI method is used for Cr(III) determination. The batch mode requires the addition of Na2CO3 when the samples were stored in acidic conditions. Choosing the experimental conditions, the determination can be selective enough for Cr(III) or Cr, Co and Ni could be totally evaluated. Different experiences were performed in order to study the total chemiluminescence signal. The aim was to check the additivity of signals in different sample conditions. Binary and ternary mixtures of the three metals stored in no acidic and acidic conditions were analysed by the FI method (Table 2). Fig. 3 shows the obtained signal recovery percentage. It can be seen that the metal mixture can be calculated as sum of individual signals. A 52 experimental design of standard mixtures was evaluated for the batch mode. A t -test showed the slopes of the different Cr(III) calibration curves obtained in the presence of different Co(II) concentrations were similar at confidence level of 95%. The same results were calculated for the slope comparison of different Co(II) calibration curves obtained in the presence of different Cr(III) concentrations. Some of those calibration equations are given in Table 6. The slope values for the mixtures were similar to those obtained when the trace element was alone. Then, the total signal could be considered as the sum of the Cr(III) and Co(II) signals. Similar studies were performed for calibration mixtures measured according to FI procedure (Table 7). In all cases, t -test showed that there was no significant difference between calibration slopes at 95% confidence interval.

The standard material reference SRM# 1640 was studied. Trace element mineral water sample was conserved in 0.5 mol l_1 HNO3 conditions. The contents of metals are given in Table 2. The analytical signal obtained by the batch mode appears in Fig. 1. Na2 CO3 was added to the standard reference material. Signal of certified standard and standard mixtures of Cr and Co reproducing the contents of SRM# 1640 was compared. Good signal recovery percentages were obtained as it can be seen in Fig. 3. Then, only the signals of the two elements contributed to the total analytical signal. Mainly the signal corresponded to Cr because the Co content considering a dilution 7/10 is near to detection limit. By the FI mode, it was possible to quantify

only Cr by adding 0.01 mol l_1 EDTA or the total contribution of the Cr, Co and Cu in the sample. To determine Cr, it was possible to use standards in acidic or non-acidic conditions in order to process samples stored in different conditions. It can be observed from the corresponding sensitivity values and the results for SRM# 1640 (diluted 6.4 times) given in Fig. 4. Without EDTA, standards and samples must be in the same conditions in order to obtain accurate estimations. Fig. 4 shows that the same results were obtained for SRM# 1640 and a mixture of Cr, Co and Cu prepared in HNO3.

4. Conclusions

A study of chemiluminescence signal has been performed for different sample storage procedures. Moreover, a parallel study of selectivity has been carried out. Calibration models of each storage protocol have been calculated in order to evaluate the influence of each storage protocol. Recovery studies have showed the signal additivity for different conditions. Selectivity, accuracy and precision also have been checked using a standard reference material.

A guideline for metal determination based on chemiluminescence signal has been proposed. The conditioning procedure of samples and standards should be chosen according to sampling strategy, analysis objectives (uni- or multi-element) and storage needs. Therefore, chemiluminescence methods by batch and FI modes can be applied for natural water stored in different conditions successfully.

When EDTA is present, it is possible the selective analysis of Cr(III) in natural water. The determination of Cr(III) is not dependent on the storage protocol working with the FI method. Then, it is possible to use standards prepared in water for processing of samples stored at different conditions, if 0.01 mol l_1 EDTA is employed as carrier. When batch mode is chosen, sample pH must be controlled adding Na2CO3.

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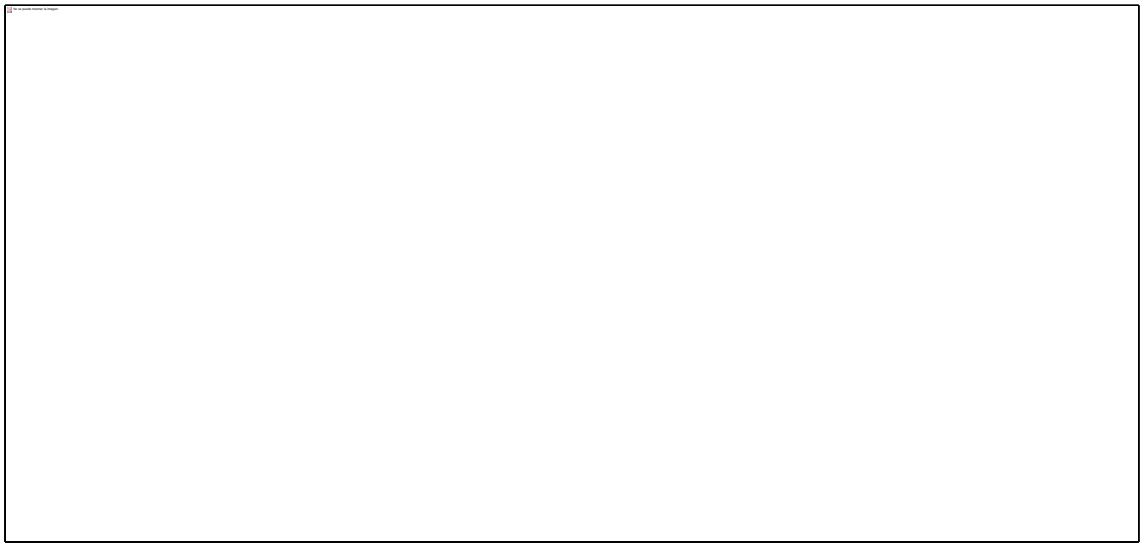

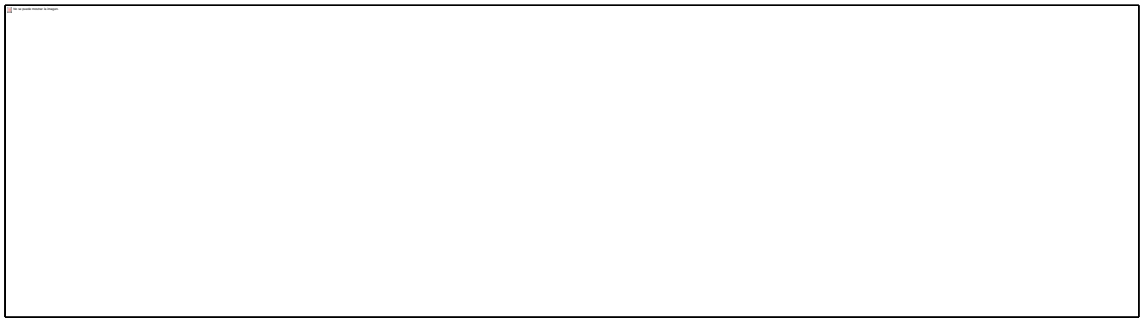

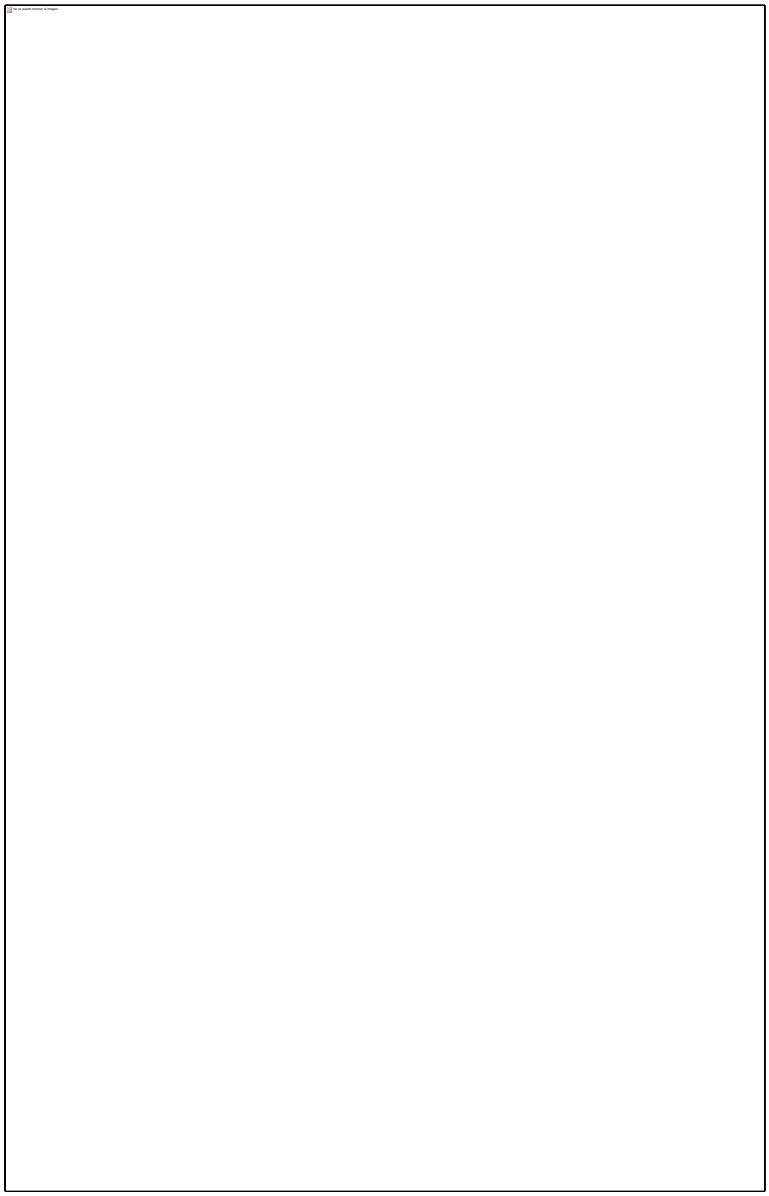

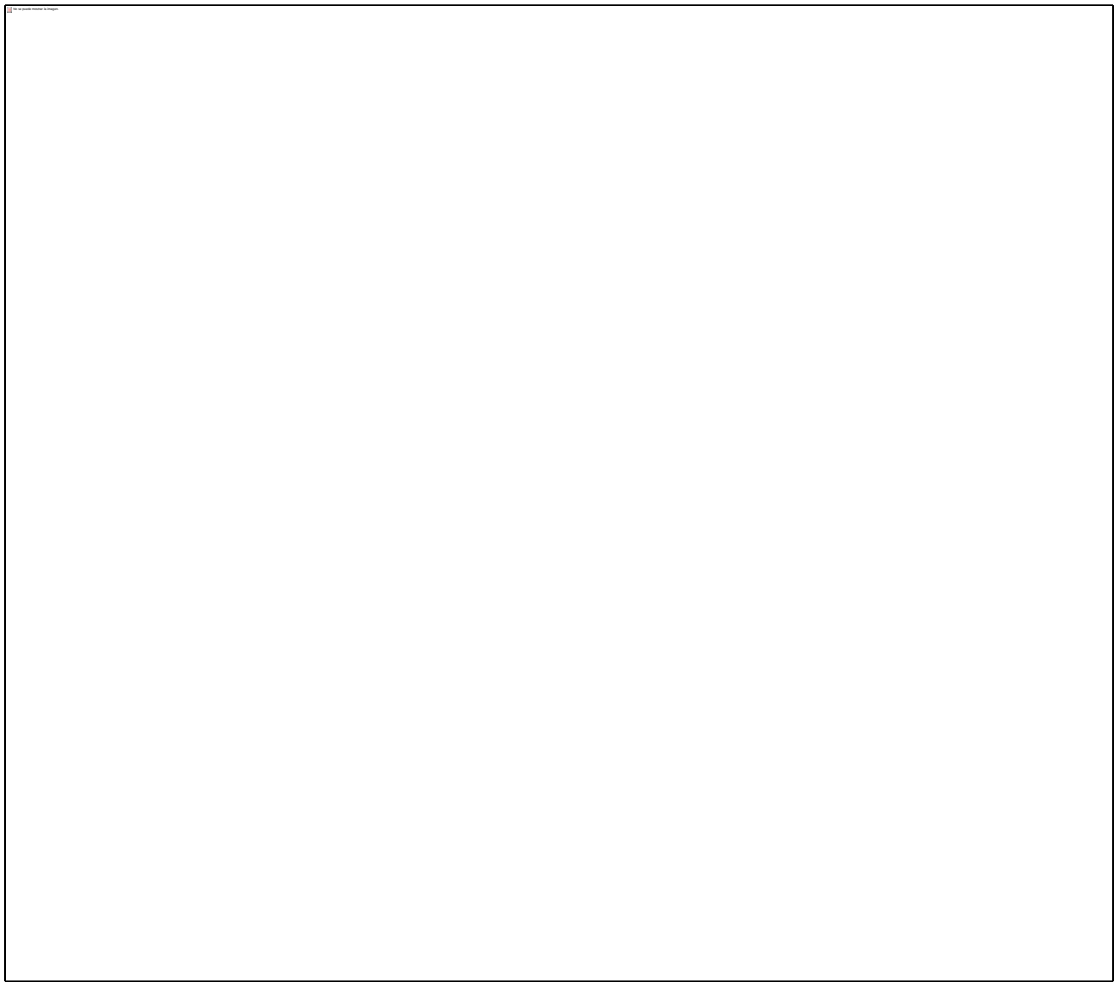

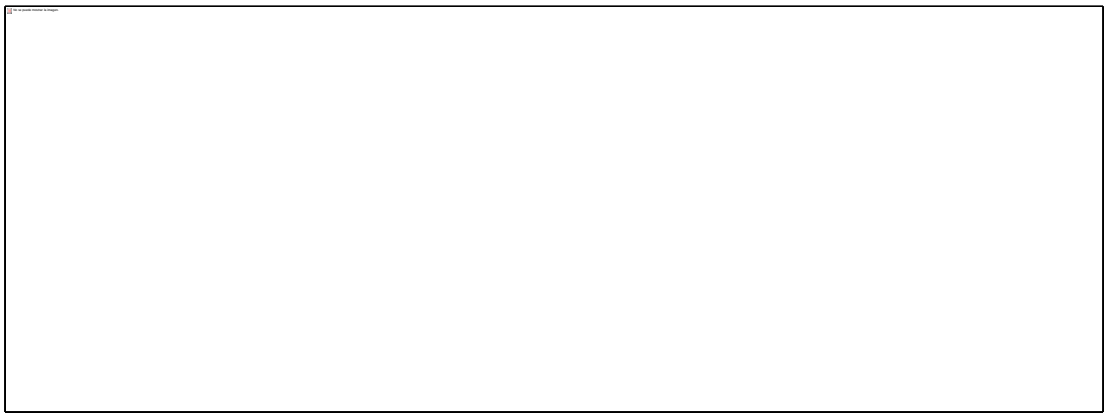
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