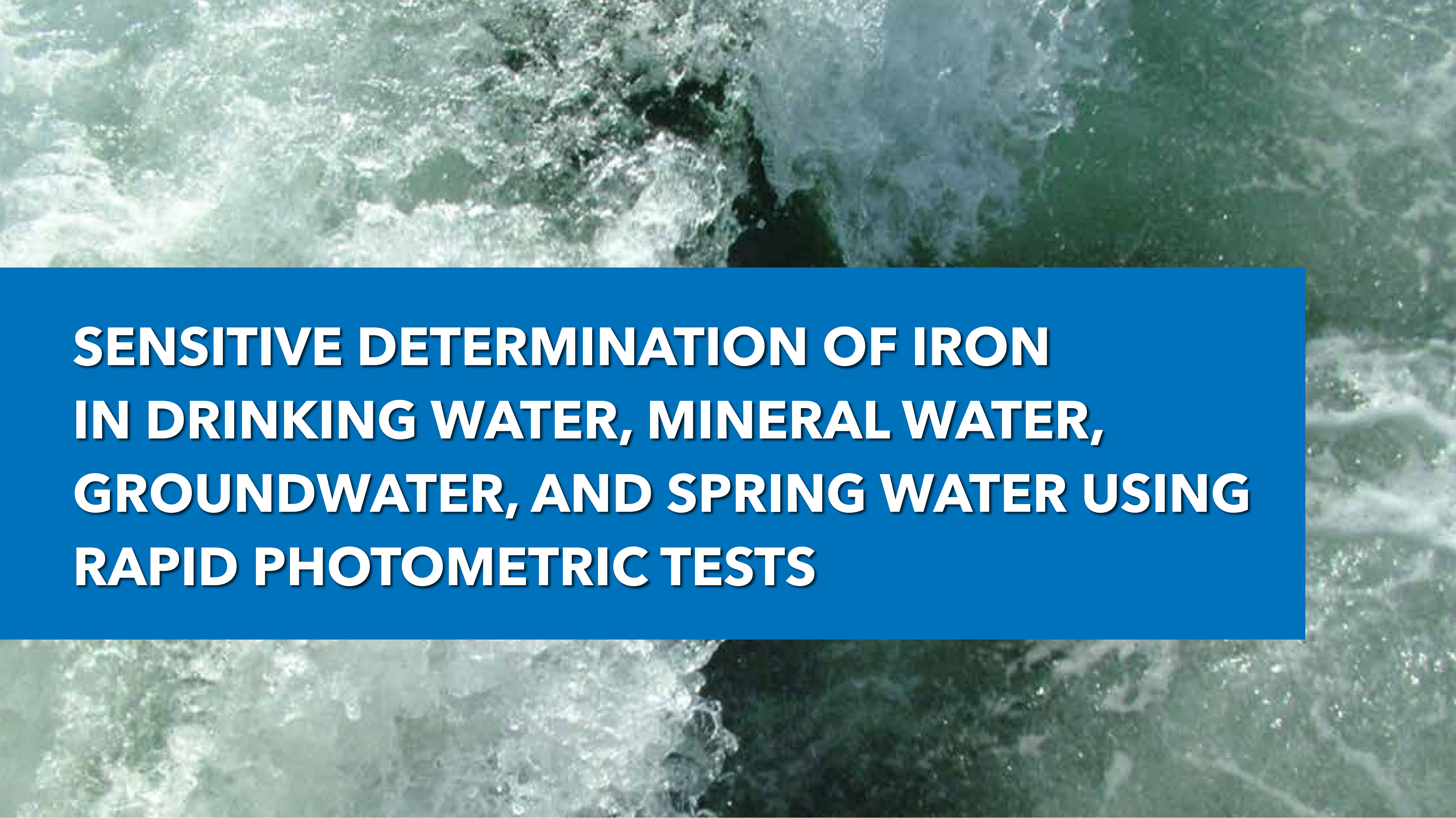


SENSITIVE DETERMINATION OF IRON IN DRINKING WATER, MINERAL WATER, GROUNDWATER, AND SPRING WATER USING RAPID PHOTOMETRIC TESTS

The quality of drinking water is regulated by a variety of quality requirements, defined; for example, in the form of limits specified by EU Council Directive 98/83 [1]. The decisive principles behind the definition of the limits – besides health-hazard aspects – also include sensory and technical reasons [2].

One example for the definitions described above is that of iron. The EU Council Directive 98/83 (version of 3 November 1998) classifies iron as an indicator parameter, i.e. in the concentrations present in drinking water, iron does not have a health-damaging effect [3]. The WHO classifies iron as follows: "Not of health concern at levels found in drinking water" [4]. Raised concentrations of iron, however, result in the formation of iron hydroxide products, which in turn form deposits in the water-pipe system and to the brown discoloration of the water coming out of the tap [5].

To safeguard the supply of clear and colorless water, country-specific limits have been set for drinking water. The limit for iron set e.g. by the EU directive is 0.2 mg/L Fe [3], while the US environmental agency, the EPA, specifies a limit for the concentration of iron of 0.3 mg/l [6].

Regarding the prevention of the formation of iron deposits in the water-pipe system, the German Technical and Scientific Association for Gas and Water (DVGW) recommends that a limit of 0.02 mg/L should not be exceeded [7].

As a measure to ensure that the specified limits and recommendations are complied with, drinking water is in many cases subjected to a treatment step in which the iron present in the water is precipitated. This method virtually eliminates any iron content, reducing the iron concentration to a level in the lower ppb range [7].

Fig. 1: Drinking water

Analytical Methods

The accurate determination of such low concentrations requires a highly sensitive analytical method. Conventional procedures that enable quantification down to the trace range include flame atomic absorption spectroscopy (flame AAS, F-AAS) and also optical emission spectrometry with inductively coupled plasma (ICP-OES). Depending on the dosage volume the measuring range of the F-AAS method according to DIN EN ISO 38406-32 is 0.002–0.020 mg/L Fe. The limit of quantification (LOQ) for the ICP-OES method according to DIN EN ISO 11885 lies at 0.002 mg/L Fe [8,9]. Measured according to the ICH Q2 standard, the ICP-MS method used at Merck achieves an LOQ of 0.0007 mg/L Fe.

Analysis of iron using analytical test kits (rapid photometric methods)

When it comes to obtaining a swift, sensitive result without having to make a high investment in instruments, rapid photometric methods offer a practical alternative.

Test kits are generally characterized by their easy handling and speed of the procedure. The choice of the type of method depends on the specific area of application, the measuring range, and the accuracy of the measurement to be achieved. In the case of iron, the user can choose between two sensitive photometric methods.

The determination of iron using the 1,10-phenanthroline method according to APHA 3500-Fe B and DIN 38406-1 enables photometric measurement down to a level of 0.01 mg/L, which is entirely sufficient for many samples [10].

In the case that iron is to be measured with a far greater degree of sensitivity, the user can select the triazine method. In this method, all iron ions are reduced to iron(II) ions. These then react in a thioglycolate-buffered medium containing a triazine derivative to produce a red-violet complex, which is subsequently determined photometrically [11]. When using a 100-mm cell and the Prove 600 UV-VIS spectrometer from the Spectroquant® Prove product range, iron concentrations as low as 0.0025 mg/L can be measured.

In the case of drinking water, such low concentrations are, due to the treatment stage and the by nature low content of iron in groundwater, not infrequently encountered.

For this reason, the user should give preference to the more sensitive triazine method in this case. Merck offers this method in the form of Spectroquant® Iron Test, Cat. No. 114761, which has an overall measuring range of 0.0025-5.00 mg/L Fe. Used in conjunction with the corresponding Spectroquant® photometers, in which the method is already pre-programmed, the time-consuming procedure for the calculation of a calibration curve can be fully omitted.

Fig. 2: Spectroquant® Prove 600

Sample preparation and performance of the measurement with Spectroquant® Iron Test 114761

Very few steps are required for preparing the sample and the actual measurement of the iron content. Samples must first be acidified with nitric acid to stabilize the iron, while carbonic acid-containing samples must also be first degassed in an ultrasound bath.

For the sensitive measurements in the 100-mm cell in the 0.0025 – 0.500 mg/L Fe measuring range, first 20 mL of the sample solution is pipetted into a suitable reaction vessel, after which 12 drops of the Fe-1 reagent are added. After a reaction time of 3 minutes, the solution is transferred to the 100-mm cell and measured in the photometer.

A detailed description of the measurement procedure is given in the application "Sensitive determination of iron in drinking water, mineral water, groundwater, and spring water". The application can be downloaded from the product page for Spectroquant® Iron Test 114761.

Measuring iron: Method comparison ICP-MS vs. Spectroquant® Iron Test 114761

In an experiment to gain an expressive statement on the suitability of the Spectroquant® test kit for the determination of the iron content in drinking and mineral water, the iron content of five different mineral waters was measured. The results were verified by reference analysis with the ICP-MS method (see Tab. 1). The LOQ of the ICP-MS method was determined according to ICH Q2, yielding a result of 0.0007 mg/L.

As Tab. 1 shows, in all mineral waters the iron content lies below the LOQ of the respective method.

Tab. 1: Iron content of mineral waters – comparison of the ICP-MS method and Spectroquant® Iron Test 114761

Mineral water	Concentration [mg/L Fe]	
	ICP-MS	Spectroquant® Iron test
Celtic natural	< 0.0007	< 0.0025
Justus Brunnen medium	< 0.0007	< 0.0025
Vitrex natural	< 0.0007	< 0.0025
Vittel natural	< 0.0007	< 0.0025
Volvic natural	< 0.0007	< 0.0025

Besides being subjected to the reference analysis procedure, the five samples were treated for analysis using the standard addition principle. Each sample was spiked with three different concentrations of iron and the respective recovery rates were determined. The results are shown in Tab. 2 and Fig. 3.

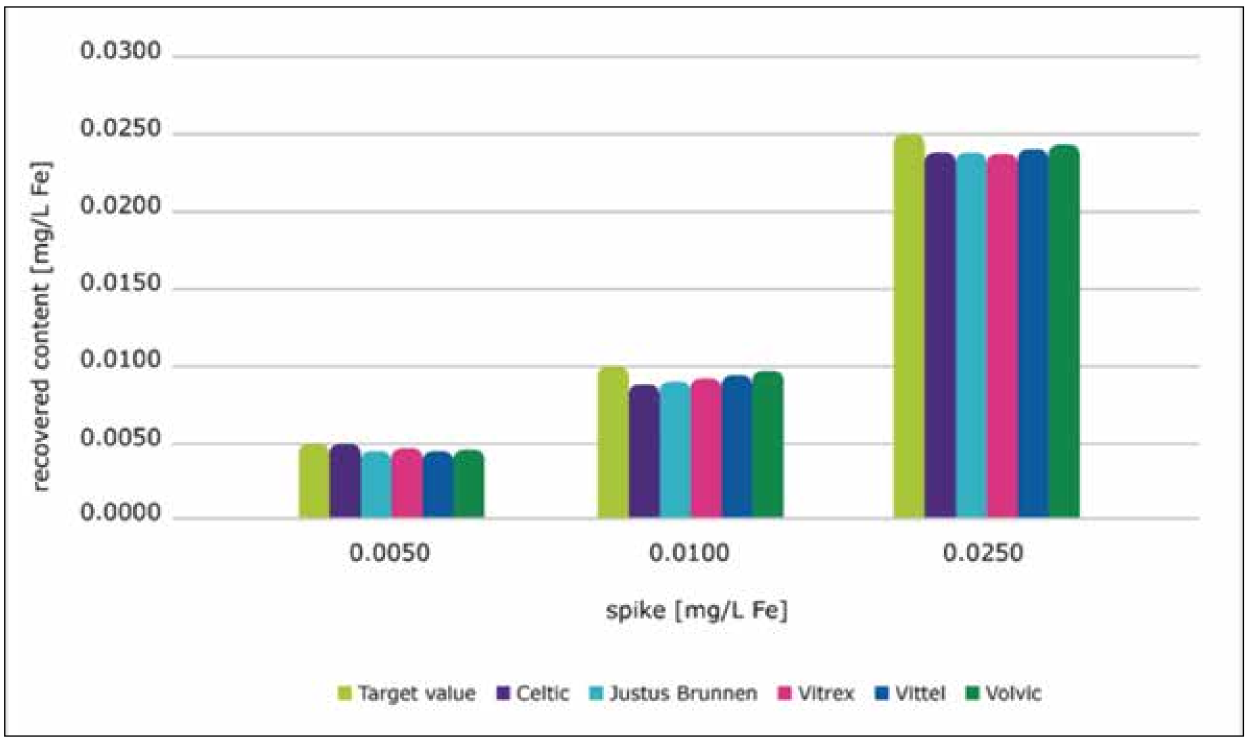
Tab. 2: Iron content recovered after standard addition

Mineral water	Addition [mg/L Fe]	Recovered concentration [mg/L Fe]	Recovery rate
Celtic natural	0.0050	0.0050	99%
	0.0100	0.0089	89%
	0.0250	0.0239	96%
Justus Brunnen medium	0.0050	0.0046	91%
	0.0100	0.0091	91%
	0.0250	0.0239	96%
Vitrex natural	0.0050	0.0048	95%
	0.0100	0.0093	93%
	0.0250	0.0238	95%
Vittel natural	0.0050	0.0046	91%
	0.0100	0.0095	95%
	0.0250	0.0241	97%
Volvic natural	0.0050	0.0047	93%
	0.0100	0.0098	98%
	0.0250	0.0244	98%

The added concentrations of iron were accurately recovered. The recovery rates in the spiked samples ranged between 89% and 99% over all experiments, with an average recovery rate of 95%.

If an even greater accuracy of the analysis is called for, the user can plot a custom calibration curve. Tab. 3 shows the performance characteristics of the pre-programmed method for Cat. No. 114761 determined according to DIN 38402 A51 + ISO 8466-1 compared against a calibration curve for the measurement range 0.0005 – 0.0100 mg/l Fe separately plotted using the test kit. The calibration curve is shown in Fig. 4.

At 4.35%, the coefficient of variation of the custom calibration curve is 3.3 times higher than that of the pre-programmed method. This is due to the fact that in relative terms deviations have a stronger effect in the lower measurement range as a result of the custom calibration. Seen in absolute terms, the custom calibration procedure can however, result in considerably lower method errors, as shown by the values of the method standard deviation and the method confidence interval for P=95%, which are 13 to 14 times lower than those of the pre-programmed method.



Tab. 3: Comparison of performance characteristics

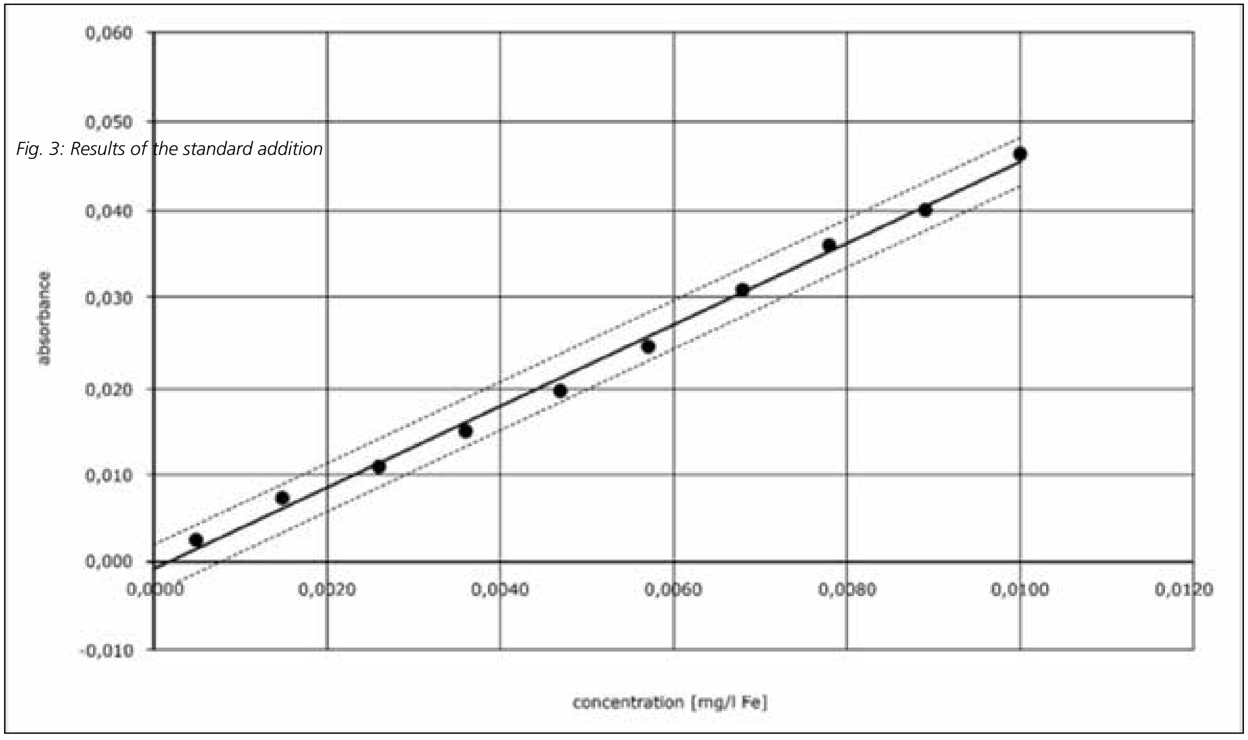


Fig. 3: Results of the standard addition

Fig. 4: Calibration curve for the measuring range 0.0005–0.0100 mg/L Fe

Tab. 3: Comparison of performance characteristics

	Pre-programmed method 0.0025 – 0.5000 mg/L Fe	Custom calibration 0.0005 – 0.0100 mg/L Fe
Method standard deviation [mg/L]	± 0.00328	± 0.00023
Method coefficient variation [%]	± 1.31	± 4.35
Confidence interval (P=95 %) [mg/L]	± 0.0079	± 0.0006

In the case of the standard additions, the use of the custom calibration resulted in a further enhancement of the recovery rate, which now achieved a mean value of 101%. The individual values lay between 95% and 106 % (see Tab. 4). Fig. 5 gives a graphic representation of the results.

Since mineral waters have only a low content of iron, the experiments were also carried out using samples of groundwater and spring water, whose iron concentrations are naturally higher due to the lack of any water treatment. The measurement was carried out using the pre-programmed method. Here too, the measurement results were verified by reference analysis using the ICP-MS method. Tab. 5 shows a comparison of the results obtained with the two methods.

The results yielded by the Spectroquant® Iron Test are in good agreement with those obtained using the ICP-MS method. Due to the very high iron content of the Bensheim groundwater sample of 2.7 mg/L Fe, in deviation from the defined procedure a 10-mm cell was used. The recovery rate here was 100%. These results show that even very high concentrations of iron can be precisely determined by means of the iron test.

Tab. 4: Iron content recovered after standard addition with custom calibration

Mineral water	Addition [mg/L Fe]	Recovered concentration [mg/L Fe]	Recovery rate
Celtic natural	0.0050	0.0053	106%
	0.0100	0.0095	95%
	0.0250	0.0255	102%
Justus Brunnen medium	0.0050	0.0049	97%
	0.0100	0.0097	97%
	0.0250	0.0255	102%
Vitrex natural	0.0050	0.0051	102%
	0.0100	0.0099	99%
	0.0250	0.0254	102%
Vittel natural	0.0050	0.0049	97%
	0.0100	0.0102	102%
	0.0250	0.0257	103%
Volvic natural	0.0050	0.0050	99%
	0.0100	0.0105	105%
	0.0250	0.0261	104%

In the case of the spring-water samples, the measurement results differed by a maximum value of 0.0008 mg/L. Even those iron concentrations that lay below the measuring range were confirmed by the ICP-MS measurements.

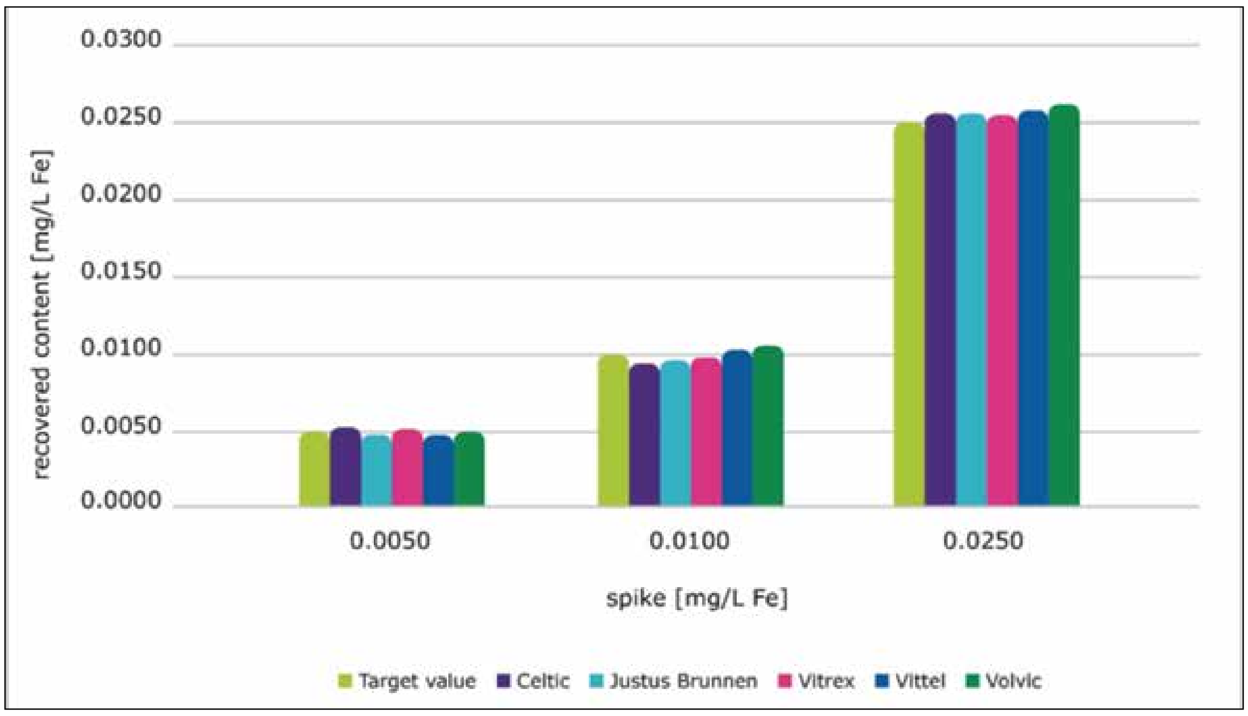


Fig. 5: Results of the standard addition with the custom calibration curve

The following list shows all chemicals and samples that were used for the application:

Designation	Supplier	Cat. No.	Batch
Spectroquant® Iron Test 0.0025-5.00 mg/L Fe	Merck	114761	HC577878
CertiPUR®			
Iron Standard 1000 mg/l	Merck	119781	HC41635381
Nitric acid 65% GR EMSURE® ISO	Merck	100456	K44274756
Water Ultrapur	Merck	101262	B1323862
Celtic naturell	La Source S.A.S.	3361730555510	22 JUL 18 06:14
Justus Brunnen medium	Ehrhardt & Sohn GmbH & Co	4104640045219	2ND: 14/09/17
Vitrex naturelle	Schwarzwald Sprudel GmbH	4007656068404	L167632156 01.02.2018
Vittel natürliches Mineralwasser	Nestlé Waters Deutschland GmbH	3179732361202	62233019P
Volvic natürliches Mineralwasser	Danone Waters Deutschland GmbH	42150237	10.08.2018 90001
Spring water Bad König	Sampling date: 29 Aug 2016		
Spring water Höchst Himmelsleiter	Sampling date: 29 Aug 2016		
Spring water Breiten-brunn	Sampling date: 29 Aug 2016		
Spring water Vielbrunn	Sampling date: 29 Aug 2016		
Spring water Raibreiten-bach	Sampling date: 29 Aug 2016		
Groundwater Bensheim	Sampling date: 29 Aug 2016		

Summary

The Spectroquant® Iron Test 114761 offers a good alternative to ICP or AAS when it comes to determining the iron content in drinking water, mineral water, groundwater, and spring water. The method yields results comparable to those obtained by the ICP-MS method and is easy to perform. For all laboratories for which the purchase of an ICP-OES or ICP-MS system is inexpedient for economic reasons, the Spectroquant® Iron Test Cat. No. 114761 offers a swift, sensitive, and precise alternative for the determination of the iron content of drinking water, mineral water, groundwater, and spring water.

Chemicals, samples, and instruments used:

All measurements were conducted using a Prove 600 instrument as per the application. The reference system used was an HR-ICP mass spectrometry method on the Element 2 device supplied by Thermo Fisher Scientific.

Tab. 5: Iron content of groundwater and spring water – comparison of ICP-MS and Spectroquant® Iron Test 114761

Groundwater and spring water	Concentration [mg/L Fe]	
	ICP-MS	Spectroquant®
Iron Test 114761		
Spring water Bad König	0.0047	0.0041
Spring water Höchst Himmelsleiter	0.0043	0.0051
Spring water Breitenbrunn	0.0022	< 0.0025
Spring water Vielbrunn	0.0017	< 0.0025
Spring water Rai-Breitenbach	0.0059	0.0051
Groundwater Bensheim	2.70	2.71

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[2] H. H. Dieter, Grenzwerte, Leitwerte, Orientierungswerte, Maßnahmenwerte – Aktuelle Defi¬ni¬tionen und Höchstwerte, Bundesgesundheitsbl 52, 1202–1206, 2009.

[3] Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human con-sumption, 1998.

[4] World Health Organization, Guidelines for Drinking Water Quality, 2011.

[5] H. D. Belitz, W. Grosch, P. Schieberle, Lehrbuch der Lebensmittelchemie, Springer Berlin Heidel-berg, 2001.

[6] United States Environmental Protection Agency, 2012 Edition of the Drinking Water Standards and Health Advisories, EPA 822-S-12-001, 2012.

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[8] DIN 38406-32:2000-05, Deutsche Einheitsverfahren zur Wasser, Abwasser- und Schlammunter-suchung – Kationen (Gruppe (E), Bestimmung von Eisen mittels Atomabsorptionsspektrometrie, 2000.

[9] DIN EN ISO 11885:2009-09, Wasserbeschaffenheit – Bestimmung von ausgewählten Elementen durch induktiv gekoppelte Plasma-Atom-Emissionsspektrometrie (ICP-OES), 2009.

[10] Package leaflet Spectroquant® Iron Test, Cat. No. 100796, June 2016.

[11] Package leaflet Spectroquant® Iron Test, Cat. No. 114761, June 2016.

The life science business of Merck operates as MilliporeSigma in the U.S. and Canada.

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