

Direct Solid Sampling by Flame Atomic Absorption Spectrometry: Determination of Manganese in Coal Samples

Érico M. M. Flores^{*,a}, José Neri G. Paniz^a, Ana Paula F. Saidelles^a, Juliano S. Barin^a,
Valderi L. Dressler^a, Edson I. Müller^a and Adilson B. Costa^b

^aDepartamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria - RS, Brazil

^bDepartamento de Biologia, Universidade de Santa Cruz do Sul, 96815-900 Santa Cruz do Sul - RS, Brazil

Um novo sistema para análise direta de amostras sólidas por espectrometria de absorção atômica com chama é proposto como alternativa para a determinação de elementos traço em carvão. Para a demonstração do potencial do procedimento a determinação de manganês foi investigada. Amostras de carvão foram moídas e pesadas diretamente em recipientes de polietileno e transportadas na forma de um aerossol seco até uma cela de quartzo posicionada entre o feixe óptico e a base do queimador. Sinais transientes foram totalmente integrados em 1 segundo. A influência das condições operacionais sobre os sinais foi estudada. Sinais de fundo foram sempre baixos e uma massa característica de 1,9 ng Mn foi encontrada. Os resultados foram considerados satisfatórios com respeito à exatidão (entre 97,5 e 103,2%) e precisão (RSD melhor que 6%). O sistema proposto é simples e pode ser facilmente adaptado a espectrômetros comerciais, permitindo a análise de mais de 80 amostras por hora.

A new device for the direct solid analysis by flame atomic absorption spectrometry was investigated as an alternative technique for the determination of trace elements in coal. The potential application of the proposed procedure for the determination of manganese was investigated. Ground coal test samples were weighed directly into polyethylene vials and carried as a dry aerosol to a slotted quartz vaporization cell placed between the flame burner and optical path. The transient signals obtained were totally integrated in 1 second. The effect of operating conditions on the analytical signal was investigated. Background signals were always low and a Mn characteristic mass of 1.9 ng was found. Results were considered satisfactory regarding to both accuracy (between 97.5 and 103.2%) and precision (RSD better than 6%). The proposed system is simple and can be easily adapted to any conventional atomic absorption spectrometers allowing the analysis of more than 80 test samples in an hour.

Keywords: flame atomic absorption spectrometry, direct solid sampling, manganese determination, coal analysis

Introduction

Since the earlier years of atomic absorption many procedures have been developed for analysis of solid samples. Nowadays, the most appropriate atomic absorption technique for this sample introduction mode is graphite furnace atomic absorption spectrometry (GFAAS).¹ Indeed, commercial accessories dedicated for the direct analysis of solid samples using GFAAS are available, and many procedures have been proposed, especially for industrial applications.²⁻⁷ Flame atomizers could be an alternative due to its low cost in comparison to graphite furnace

spectrometers, although the use of flames presents several obvious drawbacks. Nevertheless, some attempts have been made for direct solid sampling by flame atomic absorption spectrometry (DSS-FAAS). An example was the sample introduction as slurries by means of the nebulizer. However, problems related to the slurry transport and clogging of the nebulizer have been reported.⁸⁻¹²

Commercial devices have been proposed and produced (Delves cup device, total consumption nebulizer-burner, boat-in-flame technique *etc*)¹³ but none was used in a large scale. Some authors have tried to separate the vaporization step from the atomization process by separately heating the sample and transporting the delivered vapor to the flame (or to a quartz cell).¹⁴⁻¹⁷ Solid samples were also atomized in graphite tubes heated by an air + acetylene

* e-mail: flores@quimica.ufsm.br

flame for lead determination in sediment samples using a conventional atomic absorption spectrometer.¹⁸

These procedures were successful for some applications, but the introduction of solid particles directly into flames still lacks a more general procedure.

In some environmental areas the determination of trace elements in difficult matrices has become increasingly important. In these cases, procedures involving time-consuming steps, e.g., for digestion, increases the contamination and analyte loss risks and may lead to erroneous results. On the other hand, the use of concentrated acids and other reagents poses the problem of reagent disposition. Mineral coal may be cited as an example of a “difficulty sample” that must be routinely analyzed in view of its environmental importance. Interest in the industrial use of coal as a raw material in chemical plants has brought an additional need for developing methods for coal analysis, including the determination of the trace elements content in coal. Coal presents a large range of trace element concentrations, e.g., Mn, from 0.4 to 400 $\mu\text{g g}^{-1}$; Zn, from 0.5 to 1700 $\mu\text{g g}^{-1}$ and Cd from 0.01 to 9 $\mu\text{g g}^{-1}$.¹⁹ Conventional procedures for coal analysis usually involve the use of high-temperature ashing techniques in a vented furnace, followed by acid dissolution of the resulting ash with concentrated acids.²⁰ The use of microwave assisted acid digestion techniques could be an alternative. However, in this case perchloric acid addition^{21,22} is to be avoided and long heating times are still observed if special equipments, based on very high pressure and temperature conditions, are not used.

Recently a simple device was proposed for the determination of copper in bovine liver by DSS-FAAS.²³ The same device was used for cadmium determination in different biological samples.²⁴ In both cases, good performance and accuracy was observed. Based on these previous works, the present paper describes a simple and reliable procedure for the routine analysis of mineral coal. No concentrated acid is used and the sample pretreatment is reduced basically to two steps: grinding and drying. Aiming the demonstration of the proposed procedure potential, manganese determination was chosen as example.

Experimental

Instrumentation

An Analytik-Jena Model Vario 6 FL (Jena, Germany) atomic absorption spectrometer was used along this work. All measurements were carried out using deuterium background correction. A manganese hollow-cathode lamp

(wavelength of 279.5 nm, spectral slitwidth of 0.2 nm), operated at 10 mA was used as line source. A conventional burner (slit of 10 cm, air + acetylene flame) was used and the signals were evaluated by integrated absorbance (integration time = 1 s). An ultra-microbalance (Sartorius, Göttingen, Germany) Model M2P with a 1 μg resolution and a weighing range up to 2 g was also used.

The comparative procedure was performed using a microwave oven (Provecto, DGT-100, Campinas, Brazil, nominal maximum power of 1000 W), fitted with an exhaust unit. Polytetrafluorethylene (PTFE) high-pressure digestion vessels (90 mL, Provecto system) were used. Six vessels were simultaneously placed into the oven every turn. Determination of Mn in these digests was performed by GF AAS (Model EA 5, Analytik-Jena, Jena, Germany). Analytical conditions were setted according to the recommendations of the manufacturer.

The direct solid analysis system for Mn determination in coal

The device used in this work is schematically described in Figure 1. A flow meter (F) was used to control the air stream flow passing continuously through the system. A column filled with silica (placed before the flow meter entrance) was used to remove the moisture of the air flow. A glass-sampling chamber (SC) is assembled in a glass moutange made by 3 mm inner diameter tubing and two valves (V1 and V2). The glass moutange is connected to a quartz T-cell (8-mm inner diameter and 40 mm length) using a polytetrafluorethylene adapter. The cell has a 2 mm wide slot and is positioned between the optical path and the burner head along the air-acetylene flame. The quartz T-cell is adjusted to leave its slot about 8 mm below the optical path. Test samples were directly weighed (0.05 to 2.00 mg) into polyethylene (PE) vials (V). These vials were conventional autosampler cups generally used in GFAAS. Valve V2 is kept closed while the vials are carefully attached to the sampling chamber (SC) and air passes through F1 path. Valve V2 is then opened and the main air

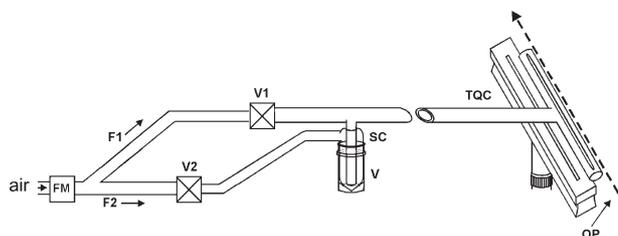


Figure 1. Proposed moutange for DSS-FAAS. FM: flow meter; V1 and V2: valves; F1 and F2: air flow path; SC: sampling chamber; V: polyethylene vial; TQC: T-quartz cell and OP: optical path.

stream is let to pass the F2 path blowing the sample contained in the PE-vial, which is carried up to quartz T-cell, where it is burnt in the flame. The total air flow-rate passing through the quartz T-cell was kept constant during all steps (6 L h^{-1}). The transient signals were completely recorded in 1 s.

Reference samples

The following coal reference materials were used in this study: NIST (National Institute of Standards and Technology, Gaithersburgh, MD, USA) SRM's 1635 and 1632b, SACCRM (South African Bureau of Standards, Pretoria, South Africa) SARM's 18, 19 and 20. Their manganese concentrations are given in Table 1. Before analysis, the samples were dried at $70 \text{ }^\circ\text{C}$ for 4 h and kept in desiccator until the manganese determination. All coal reference samples were ground in agate mortar and classified in different particle size fractions: $\leq 30 \mu\text{m}$ and $\leq 50 \mu\text{m}$ and $\leq 80 \mu\text{m}$. To minimize contamination, samples were passed through a polyester sieve in a home-made hermetic plastic container. Care was taken to minimize errors resulting from sample heterogeneity or particle segregation due to particle size.

Table 1. Manganese concentration in coal reference samples ($\mu\text{g g}^{-1}$)

Sample	Reference value
SARM 18	22 (21 to 23)
SARM 19	157 (143 to 168)
SARM 20	80 (77 to 82)
NIST SRM 1632b	12.4 ± 1.0
NIST SRM 1635	21.4 ± 1.5

Sample digestion

The comparative digestion procedure was adapted from that described by Bettinelli and co-workers.²⁵ Test-samples from 100 to 150 mg were weighed and 10 mL of the aqua regia, and 5.0 mL hydrofluoric acid were added. After 1 h for initial acid attack the PTFE vessels were capped and heated by the following program in the microwave oven: 8 min at 300 W, 4 min at 600 W and 7 min at 480 W. Final digests were diluted with water to 50 mL and further analyzed by GFAAS.

Results and Discussion

Operating conditions optimization for the proposed DSS-FAAS device

Tests were initially performed to evaluate the influence

of the quartz T-cell distance to the optical path as well as the effect of flame composition on the absorbance signals. The SARM 19 reference sample (masses between 0.15 and 0.30 mg) was initially used in this study. Later on, the other reference samples were also investigated but no differences were observed. Integrated absorbance signals were converted to characteristic mass to facilitate the signals comparison and the distance between the quartz T-cell and the burner was kept at 5 mm. The sample particle size was $\leq 50 \mu\text{m}$. Figure 2 shows the results for three investigated distances: 3, 6 and 8 mm. An evident decrease of the characteristic mass from 3 to 6 mm is observed while from 6 to 8 mm this figure varies only from 2.7 to 2.2 ng with relative standard deviation of 4 and 6.5%, respectively. The distance of 8 mm was then chosen in view of its better sensitivity and lower relative standard deviation. This distance was the largest attained due to the limit of the mechanical parts of the equipment.

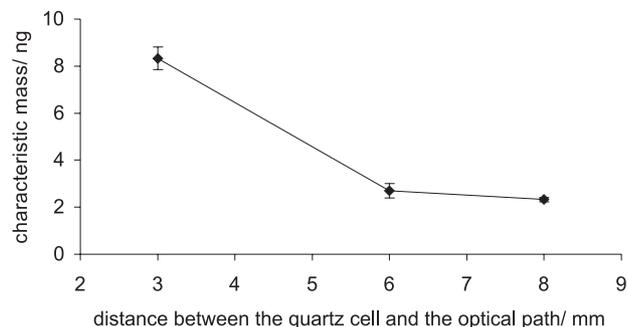


Figure 2. Influence of distance between the quartz T-cell and the optical path on the characteristic mass for Mn determination in a coal sample (SARM 19). Flame composition: air (10 L min^{-1}) and acetylene (2 L min^{-1}); air flow in the sampling chamber: 6 L min^{-1} ; distance between the burner and quartz T-cell: 5 mm; particle diameter $\leq 50 \mu\text{m}$; bars represent the relative standard deviation ($n = 5$).

The flame composition influence on Mn signals is shown in Figure 3. For these studies the acetylene flow was kept constant at 2 L min^{-1} and the air flow was varied between 8 and 12 L min^{-1} . Characteristic masses ranged from 2.0 to 9.2 ng Mn . The best (lower characteristic mass) were obtained for the 10 L min^{-1} air flow. More oxidizing flame conditions led to a clear signal decrease and larger relative deviations. With fuel richer flames no significant improvement was observed. Then, the $2 + 10 \text{ L min}^{-1}$ acetylene + air mixture was chosen for the further experiments. Possible memory effects were evaluated using empty vials after sample measurements, and showed to be insignificant.

Background signals were always low (lower than 0.06 in peak height scale) for all investigated air flow rates. For the selected conditions the relative standard deviation was considered good (better than 6%).

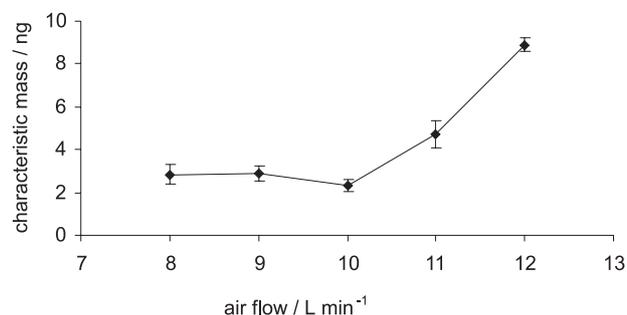


Figure 3. Influence of flame composition (acetylene flow, 2 L min⁻¹) on the Mn characteristic mass in a coal reference sample (SARM 19). Air flow in the sampling chamber: 6 L min⁻¹; distance between the burner and quartz T-cell: 5 mm; distance between the optical path and the quartz T-cell: 8 mm; particle diameter $\leq 50 \mu\text{m}$; bars represent the relative standard deviation ($n = 6$).

Influence of particle size on signals by flame-DSS

The investigated coal reference samples were classified in three granulometric fractions: ≤ 30 , ≤ 50 , and $\leq 80 \mu\text{m}$. It was observed that for the finer fractions ($\leq 30 \mu\text{m}$ and $\leq 50 \mu\text{m}$) the signals were quite similar for all studied coal samples. Only a slight increase of the absorbance signal (7%) was observed for the $\leq 30 \mu\text{m}$ particle size fraction. However, when the $\leq 80 \mu\text{m}$ fraction was used some difficulties related to the effective sample transport and eventual memory effects were experienced. In addition, the absorbance signals presented a small decrease (about 25%) that could be attributed to the reasons cited above. Then, the $\leq 50 \mu\text{m}$ particle size was chosen for all coal reference samples. For routine analysis it is an important point once excessive sample grinding increases the risks of contamination or analyte losses and turns this step more time consuming. At the optimized conditions reproducible signals and surprisingly low background signals were observed. Figure 4 shows typical Mn atomic and background signals using the proposed DSS-FAAS system.

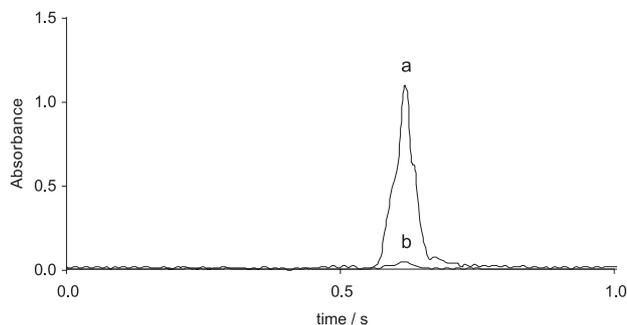


Figure 4. Typical absorbance profiles for (a) Mn atomic signal and (b) background for 0.15 mg of a reference coal (SARM 19) by the proposed system with optimized conditions. Flame composition: air (10 L min⁻¹) and acetylene (2 L min⁻¹); air flow in the sampling chamber: 6 L min⁻¹; distance between the burner and quartz T-cell: 5 mm; distance between the optical path and quartz T-cell: 8 mm; particle diameter $\leq 50 \mu\text{m}$.

Calibration

Calibration in direct solid GFAAS analysis may still represent an important challenge in view of the difficulties related to the direct comparison with liquid reference solutions and the proper use of chemical modifiers. In DSS-FAAS the comparison with aqueous solutions should be almost impossible. Thus, calibration for DSS-FAAS should involve different masses from a chosen reference material or similar masses of several different solid reference samples.

In the present work analytical curves were established using three coal reference samples (SARM 18, SARM 19 and SRM 1632b). Figure 5 presents the good correlation between the different Mn masses relative to the three reference materials and their respective integrated absorbance signals ($r=0.9988$). The curve contains 30 points (minimum of 7 points for each test sample) each one representing a single measurement. Taking the two other coal reference samples (SARM 20 and SRM 1635) as unknowns and using this curve for calibration the agreement between found and certified values ranged from 97.5 and 103.2% ($n=7$). In addition, the same samples were analysed using the described comparative acid digestion procedure.²⁵ Results obtained by this and the proposed procedures are shown in Table 2, and they agree better than 95%. It is worth of note that the investigated coal reference samples belong to different coal classifications (betuminous, sub-betuminous, etc); thus

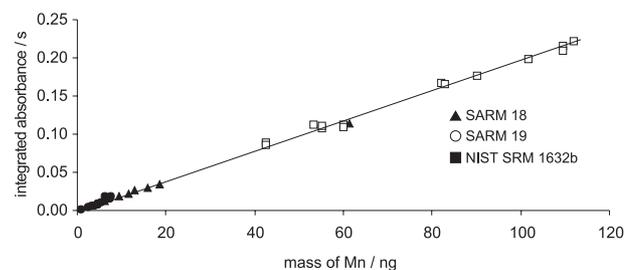


Figure 5. Correlation between Mn absorbance and Mn mass in different coal certified reference samples using the proposed procedure ($y = 0.002x + 0.0009$; $R^2 = 0.9977$). All masses were between 0.05 and 2.00 mg.

Table 2. Mean values ($\mu\text{g g}^{-1}$) and standard deviation for determination of Mn in coal reference samples by conventional acid digestion and by proposed system ($n=7$)

Reference sample	Certified value	Procedure	
		Proposed system	Acid digestion ^a
SARM 20	80 (77 to 82)	78.0 \pm 4.6	78.9 \pm 2.0
NIST SRM 1635	21.4 \pm 1.5	22.1 \pm 1.3	21.0 \pm 0.9

^aDetermination by GFAAS, according to procedures described in reference 25.

different coal classes can be analysed by the proposed procedure if ground to $\leq 50 \mu\text{m}$ particle size. The relative standard deviations were better than 6% ($n=7$). These results were considered satisfactory taking into account the small masses taken and the heterogeneity of the coal samples.

Figures of merit

Table 3 presents the analytical figures of merit and some optimized conditions of the proposed DSS-FAAS procedure. A characteristic mass of 1.9 ng/0.0044 s was obtained for sample masses ranging from 0.05 to 2 mg. Concerning the sample homogeneity it was observed that it did not represent a limitation to the proposed procedure. The calculated instrumental limit of detection was 1.1 ng (3 s, $n=14$) or $1.1 \mu\text{g g}^{-1}$ if a sample mass of 1 mg is used. This limit of detection may be sufficient for routine determination of Mn in coal samples. Relative standard deviations were about 6%, of the same magnitude for those found for solid sampling methods by GFAAS.^{26,27} Drying and keeping the sample in a dry environment was necessary to minimize problems related to sample agglomeration and particle retention on the internal surfaces of the system during the transport to the quartz T-cell. Concerning the sample throughput, it was possible to perform more than 80 determinations per hour after weighing the sample.

Table 3. Figures of merit and optimized conditions for the proposed DSS-FAAS procedure

Parameters	
Limit of detection	1.1 ng (absolute)
Characteristic mass	1.9 ng/0.0044 s
Air flow in the sampling chamber	6 L min ⁻¹
Flame composition	air: 10 L min ⁻¹ and C ₂ H ₂ : 2 L min ⁻¹
Distance between quartz T-cell and burner	5 mm
Distance between quartz T-cell and optical path	8 mm
Particle size	$\leq 50 \mu\text{m}$
Relative standard deviation	< 6.0 % ($n=7$)

In this work background signals were always low and the use of the deuterium corrector was sufficient, similarly to a previous work using a similar device.^{23,24} A limitation of the proposed procedure is the maximum sample mass, restricted to 2 mg. This limits the concentration limit of detection and may represent a problem if very inhomogeneous samples are to be analysed. On the other hand, the procedure used an easy made and non-expensive assembly coupled to a conventional flame atomic

absorption spectrometer. The time-consuming coal digestion step is overcome, coal samples are easy to grind and total analysis time is competitive to the conventional procedures. Such characteristics turn the proposed procedure feasible alternative with respect to Mn determination in coal samples.

Acknowledgements

Authors thank to UFMS, FAPERGS and CNPq, for supporting this study.

References

- Kurfürst, U.; *Solid Sample Analysis*, Springer Verlag: Berlin, 1998.
- Krivan, V.; Dong, H.M.; *Anal. Chem.* **1998**, *70*, 5312.
- Hornung, M.; Krivan, V.; *Spectrochim. Acta Part B* **1999**, *54*, 1177.
- Nowka, R.; Marr, I.L.; Ansari, T.M.; Muller, H.; *Fresenius J. Anal. Chem.* **1999**, *364*, 533.
- Lucic, M.; Krivan, V.; *J. Anal. At. Spectrom.* **1998**, *13*, 1133.
- Nowka, R.; Muller, H.; *Fresenius J. Anal. Chem.* **1997**, *359*, 132.
- Friese, K.C.; Krivan, V.; *Spectrochim. Acta Part B* **1998**, *53*, 1069.
- Alves, F.L.; Smichowski, P.; Farías, S.; Marrero, J.; Arruda, M. A.Z.; *J. Braz. Chem. Soc.* **2000**, *11*, 365.
- Willis, J.B.; *Anal. Chem.* **1975**, *47*, 1752.
- Fuller, C.W.; *Analyst* **1976**, *101*, 961.
- Harrison, W.W. Juliano, P.O.; *Anal. Chem.* **1971**, *43*, 248.
- Kashiki, M.; Petrucci, G.; Van Loon, J.C.; *Fresenius' Z. Anal. Chem* **1987**, *326*, 345; Oshima, S.; *Anal. Chim. Acta* **1970**, *51*, 387.
- Welz, B.; Sperling, M.; *Atomic Absorption Spectrometry*, 3rd ed., Wiley-VCH: Weinheim, 1999, pp. 20-26.
- Magalhães, C.E.C.; Krug, F.J.; Fostier, A.H.; Berndt, H.; *J. Anal. At. Spectrom.* **1997**, *12*, 1231.
- Berndt, H.; *Spectrochim. Acta Part B* **1984**, *39*, 1121.
- Campos, R.C.; Curtius, A.J.; Berndt, H.; *J. Braz. Chem. Soc.* **1990**, *1*, 66.
- Campos, R.C.; Curtius, A.J.; Berndt, H.; *J. Anal. At. Spectrom.* **1990**, *5*, 669.
- Alvarado, J.; Jaffe, R.; *J. Anal. At. Spectrom.* **1998**, *13*, 297.
- Swaine, D.J.; Goodarzi, F.; *Environmental Aspects of Trace Elements in Coal – Energy and Environmental*, Kluwer Academic Publishers: Dordrecht, 1995, vol. 2, p. 313.
- Pollock, E.N. In *Trace Elements in Fuel*; Babu, S.P., ed., American Chemical Society: Washington-DC, 1975, pp. 23-24.
- Fadda, S.; Rivoldini, A.; Cau, I.; *Geostandards Newslett.* **1995**, *19*, 41.

22. Lachas, H.; Richaud, R.; Jarvis, K.E.; Herod, A.A.; Dugwell, D.R.; Kandiyoti, R.; *Analyst* **1999**, *124*, 177.
23. Flores, E.M.M.; Costa, A.B.; Barin, J.S.; Dressler, V.L.; Paniz, J.N.G.; Martins, A.F.; *Spectrochim. Acta Part B* **2001**, *56*, 1875.
24. Flores, E.M.M.; Paniz, J.N.G.; Martins, A.F.; Dressler, V.L.; Müller, E.I.; Costa, A.B.; *Spectrochim. Acta Part B* **2002**, *57*, 2187.
25. Bettinelli, M.; Baroni, U.; Pastorelli, N.; *J. Anal. At. Spectrom.* **1987**, *2*, 485.
26. Belarra, M.A.; Resano, M.; Vabhaecke, F.; Moens, L.; *Trends Anal. Chem.* **2002**, *21*, 828.
27. Huang, M. D.; Krivan, V.; *Fresenius J. Anal. Chem.* **2000**, *368*, 227.

Received: August 30, 2002

Published on the web: February 27, 2004