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Original Research

Long-Term Measurements of CFCs and SF_6 Concentrations in Air

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Abstract

The influence of Montreal Protocol legislation accepted by Polish Authority (in 2002) on concentration halogenated compounds (CFCs) in the atmosphere was observed. We present measurements made on atmospheric concentrations of seven halogenated compounds (freons F-11, F-12, F-113, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, and sulphur hexafluoride) between 1997 and 2008 from the densely polluted urban area of Kraków. The trend coefficients are calculated for the mean daily data measurements obtained at the Kraków stations (50ºN, 20ºE) using weighted regression method. The concentration of F-11, chloroform, 1,1,1-trichloroethane, and F-12 has a tendency to decrease, whereas F-113, carbon tetrachloride, and sulphur hexafluoride tend to increase. The results of the trend coefficient calculations expressed in ppt/year are F-11, -3.2; F-113, +0.4; $CHCl_3$, -1.3; CH_3CCl_3, -3.5; CCl_4, +1.9; F-12, -0.6; and SF_6, +0.22. The result of the measurements, particularly after 1 July 2002, shows a decrease in concentration of the mentioned compounds. This suggests that the Montreal Protocol limitations of CFC emissions are respected in Central Europe, especially in Poland, where those limitations have been in place since July 2002.

Keywords: trace gases, chlorofluorocarbons, gas chromatography, ECD, long-term measurements in the urban area

Introduction

The concentration of chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) in the atmosphere are at ppt level (ppt = 10^{-6} ppm). As radiatively active gases they influence the depletion of the Earth's ozone layer and increase the greenhouse effect. The hypothesis about destruction of the Earth's ozone layer by freons was introduced by Rowland and Molina in 1974 [1]. The potential possibility of the destruction of the Earth's ozone layer by anthropogenic chlorofluorocarbons increased the anxiety of the international community enough to lead to greater protection of the natural environment. International cooperation caused freon production and emissions to the atmosphere to became almost entirely discontinued (Montreal Protocol, 1987). In 1995 S. Rowland, M. Molina, and P. Crutzen received the Nobel Price in chemistry for explaining the chemical processes that influence the ozone layer. This discovery prevented an ecological crisis with potentially catastrophic after-effects. Important historical facts concerning protection of the ozone layer are presented in Fig. 1. The decisions of the Vienna Convention (1985) and of the Montreal Protocol (1987) mandate a 50% reduction in the World's emissions of CFCs between 1986 and 2004.

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In addition, they also suggest a total reduction of CFC emissions to the atmosphere by the year 2030. The Advanced Global Atmospheric Gas Experiment (AGAGE) program measurements of global CFC concentration trends in the atmosphere indicate that the limitations of the world production of CFCs has resulted in a decrease of the atmospheric concentration of several investigated compounds [1]. However, measurements of sulphur hexafluoride (SF_6) concentrations in the atmosphere indicate that its concentration is still growing [2]. Available data indicate that there are significant pollution events in the vicinity of large urban areas [3]. A good fraction of these events are caused by the use of SF_6 by the electrical power industry in high-voltage gas-insulated switchgears (GISs) and transmission lines from where it leaks into the atmosphere. Since urban centers have high population densities and large cumulative demand for electricity, there are also more GISs in and near these areas and more sources delivering SF_6 to the atmosphere [3].

CFC and SF_6 measurements in the atmosphere are usually carried out at the so-called clean stations situated far from urban areas. Such a clean station in Europe is situated at Mace Head (Ireland) and has been participating in the AGAGE program since 1987 [4]. The reason for monitoring CFC pollutants at such places is that the global change in CFCs are independent of local emissions. It would, however, be interesting to compare these global concentration changes with their variations in urban areas [5]. In central Europe such measurements have been carried out in Kraków since 1997 [6]. Kraków is situated 100 km East of the highly polluted, industrial area of Silesia. Finally, these investigations can show whether the Montreal Protocol limitations are respected in this part of Europe, especially in Poland, where those limitations were implemented in July 2002 [7].

CFCs and SF_6 also are used in hydrogeology as tracers for age-dating of young groundwaters. Such measurements have been carried out in the UK's two largest cities (London and Birmngham) and a smaller urban area, Bristol [8]. Furthermore, Kraków's outpost is engaged in such investigations [9]. From this point of view, measurements of CFCs and SF_6 in the atmosphere are very important, because in urban environments with many CFCs, point sources uncertainties in the delivery of CFCs to groundwater complicate interpretation of observed CFC distributions [10].

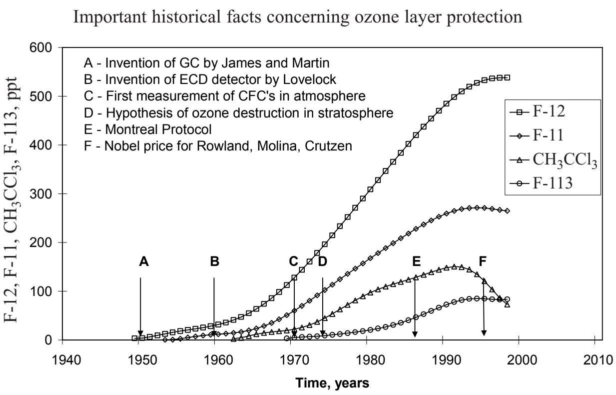

Fig. 1. The concentration of CFCs in 1950-2000 on the historical facts concerning protection of the Earth's ozone layer.

Experimental Procedures

Measurements of the concentrations of seven halogenated compounds, i.e. freons F-11 ($CFCl_3$), F-12 (CF_2Cl_2), F-113 (CCl_2FCClF_2), chloroform ($CHCl_3$), 1,1,1-trichloroetane (CH_3CCl_3), carbon tetrachloride (CCl_4) and SF_6 have been carried out in the densely populated urban area of Kraków between 1997-2008. The measurement of the indicated compounds are conducted with a computer-controlled two-channel gas chromatograph (GC Fisons, type 8000) equipped with both channels and electron capture detectors (ECD) working in a constant current mode [11]. In each channel, two columns are used, working in a back flush system. In the first channel, where F-11, F-113, $CHCl_3$, CH_3CCl_3 and CCl_4 are analyzed, the stainless steel columns are filled in with 10% SP 2100, 80/100 mesh, 2 mm in diameter, 2- and 10-ft. long. In the second channel, where SF_6 and freon F-12 are analyzed, the stainless steel columns are filled with molecular sieve 5A, 80/100 mesh, 4 mm in diameter, 1- and 3-m long. The temperature of column operation is 55ºC and the temperature of detectors in both channels is 300ºC. The detection limit of the detectors calculated as double amplitude of noise level is: F-11, 1.2±0.7 ppt; F-113, 6.2±0.9 ppt; $CHCl_3$, 16.2±2.7 ppt; CH_3CCl_3, 6.7±0.9 ppt; CCl_4, 2.9±0.6 ppt; F-12, 5.7±2.6 ppt and; SF_6, 0.15±0.08 ppt.

The air samples are sucked from the roof of two different laboratory buildings Institute of Nuclear Physics. The air samples were dried in a Nafion tube. The unknown air sample and standard sample containing a known concentration of the indicated compounds were injected to GC alternatively every 30 minutes. The chromatograms of air and standard samples are registered by a ChemStation of the Hewlett Packard computer program. As a standard, a cylinder filled with air produced by LINDE Plc was used. This secondary standard was calibrated relative to the primary standard of the Scripps Oceanography Institute, San Diego, USA (SIO-1993 scale). Primary standard contained the following concentration of chlorofluorocarbons: F-11, 264.87±0.089 ppt; F-113, 83.43±0.152 ppt; $CHCl_3$, 17.24±0.441 ppt; CH_3CCl_3, 97.45±0.235 ppt; CCl_4, 97.78±0.176 ppt; F-12, 533.52±0.258 ppt; and SF_6, 3.942±0.019 ppt. During the measurements, nine cylinders filled with air as secondary standard were prepared.

Results and Discussion

A typical monthly record of temporary data measurements of the concentration of the CFCs in air samples is calculated from the registered area of each of the chromatographic peaks corresponding to the components of the sample and the standard. The concentrations of the compounds were calculated using the five-point Lagrange's interpolation method that allows determination of detector sensitivity at the moment of air sample analysis. The procedure significantly improves measurement accuracy [12]. From a temporary measurement data, the daily and monthly arithmetic mean concentration values and its standard deviations are calculated.

Figs. 2 to 8 depict daily mean values and monthly mean values (black line) for the concentration of F-11, F-113, $CHCl_3$, CH_3CCl_3, CCl_4, F-12, and SF_6 measured in Kraków (Poland). The data from Kraków presented in the figures are converted to the SIO-2005 scale [13]. The daily-calculated concentration data indicate that the sudden increase of the CFCs concentration appears against the usual background level of these concentrations. The greatest changes of the concentration, reported for F-113, $CHCl_3$, and CCl_4 (Figs. 3, 4, and 6), are probably related to the use of these solvents at dry-cleaning facilities. The incidental changes of CFC concentrations, mentioned above influence the mean monthly values of these concentrations as is seen in the figures.

Figs. 2-8, illustrate regression curves in the form y=a+bx calculated using the weighted regression method (dashed line), to estimate the tendency for changes in concentration of the fluorocarbons in Kraków. For approximation of CH_3CCl_3 and F-12 data the exponential function and quadratic function have been used, respectively. The yearly tendency in the concentration (b, ppt/year) can be calculated from the formula given by Taylor [14], as well as parameter (a, ppt) for the equation of the line for weighted linear regression. Table 1 shows the values of coefficient (b) in time period of July 1997 to May 2008 and parameter (a) calculated for 1 July 1997, when measurements were started. It can be seen clearly from Figs. 2-8 that the concentration of CFCs, measured in urban areas of Kraków, are characterized by seasonal variability. In the background of these changes four compounds – i.e. F-11, F-12, $CHCl_3$, and CH_3CCl_3 – have a tendency to decrease, but for F113, CCl_4, and SF_6 concentrations increased (Table 1). Compounds F113, $CHCl_3$, and CCl_4 are characterized by higher seasonal variability of concentration amplitude than the other compounds.

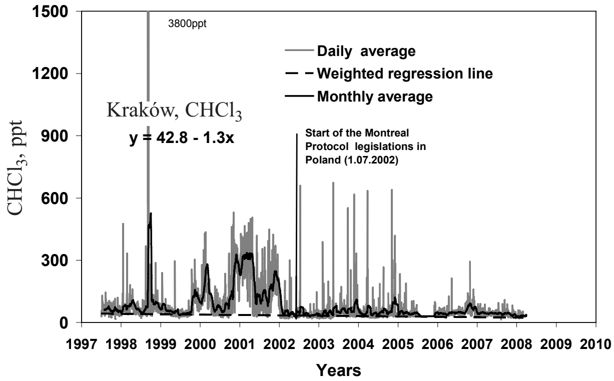

Fig. 4. As in Fig. 2, for $CHCl_3$.

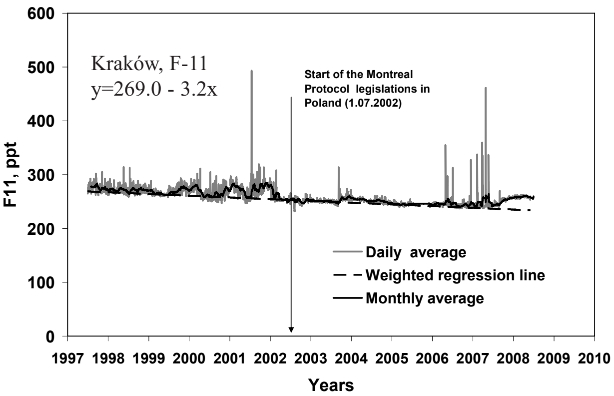

Fig. 2. The daily mean value and monthly mean value of F-11 concentration, measured in Kraków 01.07.1997 to 31.05.2008. Regression lines y = a + bx were calculated using the weighted regression method.

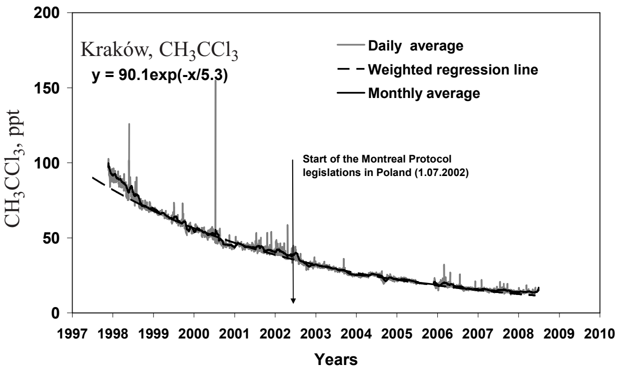

Fig. 5. As in Fig. 2, for CH_3CCl_3. Weighted regression line is exponential function.

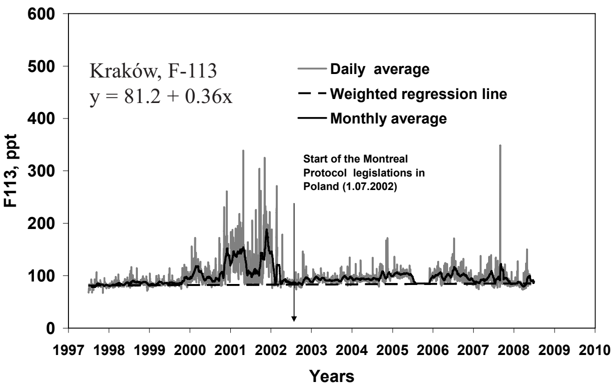

Fig. 3. As in Fig. 2, for F-113.

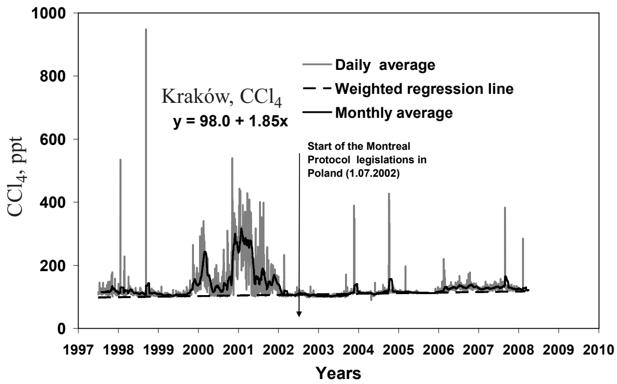

Fig. 6. As in Fig. 2, for CCl_4.

Table 1. Yearly trend coefficient (b) from 07.1997 to 05.2008 and parameter (a) calculated in 1.07.1997 (using linear function y=a+bx).

Station	Kraków, Poland (50ºN, 20ºE, 250 m above MSL)	
Compound	b, ppt/year	a, ppt
F-11	-3.2 ± 0.1	269.0 ± 0.3
F-113	+ 0.4 ± 0.1	81.2 ± 0.2
$CHCl_3$	- 1.3 ± 0.2	42.8 ± 0.9
CH_3CCl_3*	- 3.5 ± 0.2	35.8 ± 0.3
CCl_4	+1.9 ± 0.1	98.0 ± 0.5
F-12*	-0.6 ± 0.1	546.5 ± 0.6
SF_6	+0.22 ± 0.01	4.04 ± 0.01

* (b) from the period 07.2002 to 05.2008 and (a) calculated in 1.07.2002.

The increase of investigated compound concentrations is probably connected with the wind directions over Poland, i.e. with advection under Kraków air mass from the Western part of Poland or Europe, as presented in Fig. 9. Fig. 9 illustrates the frequency of air mass advection and wind frequency over the Kraków area. The observed concentration increases during the winter seasons indicate that they have origins outside the Kraków region.

Figs. 2-8 present an interesting diminishing frequency of the seasonal variability of CFC concentration amplitudes after 1 July 2002, when the Montreal Protocol legislation was implemented in Poland [7]. This suggests that the most observed CFC pollution events have been emitted from sources localized on Polish territory, because the wind and air mass movements (Fig. 9) still have the same statistical character in Kraków region, as before legislation implementation. In Fig. 9 the time period 1961-90 and 1997-2008 (black solid line) are compared. Observed diminishing seasonal variability of CFC concentration amplitudes suggest that CFC emission limitations posed by the Montreal Protocol are respected in Poland.

Conclusions

This paper presents a general view of environmental pollution of Kraków air by selected halocarbons, i.e. freons F-11 ($CFCl_3$), F-12 (CF_2Cl_2), and F-113 (CCl_2FCClF_2), chloroform ($CHCl_3$), 1,1,1-trichloroetane (CH_3CCl_3), carbon tetrachloride (CCl_4), and SF_6. In spite of the constant amendment of Kraków air quality, the state of the atmosphere needs new measurements for reducing pollutant emissions.

The chlorofluorocarbons emitted in Kraków are the result of the superposition of the concentration of these compounds typical for this part of Europe and local, incidental concentration fluctuations.

The measured concentrations of CFCs are characterized by seasonal variability. On the background of these changes, F-11, F-12, $CHCl_3$, and CH_3CCl_3 have a tendency to decrease, whereas F-113, CCl_4, and SF_6 concentrations tend to increase (Table 1).

Particular attention should be given to new investigations as to the origin of CFCs from the West, because an increase of halocarbon concentrations in winter months correlates with air mass advection from this region.

The observed diminishing frequency of the seasonal variability of CFC concentration amplitudes after the date of 1 July 2002, when the Montreal Protocol legislation was implemented in Poland, suggest that the limitations of CFCs emissions in Poland are adhered to.

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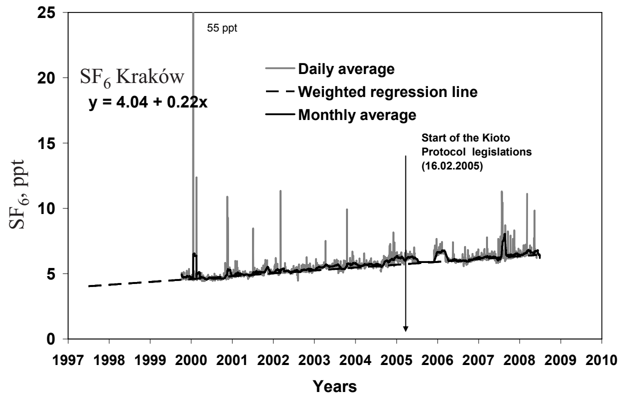

Fig. 7. As in Fig. 2, for SF_6, but period of measurements is 1.10.1999 to 31.05.2008.

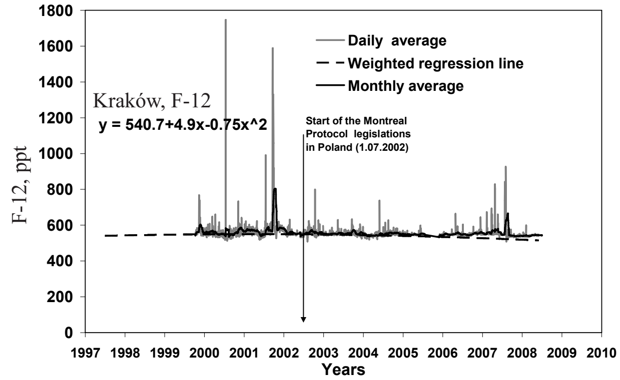

Fig. 8. As in Fig. 2, for F-12, but period of measurements is 1.10.1999 to 31.05.2008. Weighted regression line is a quadratic function.

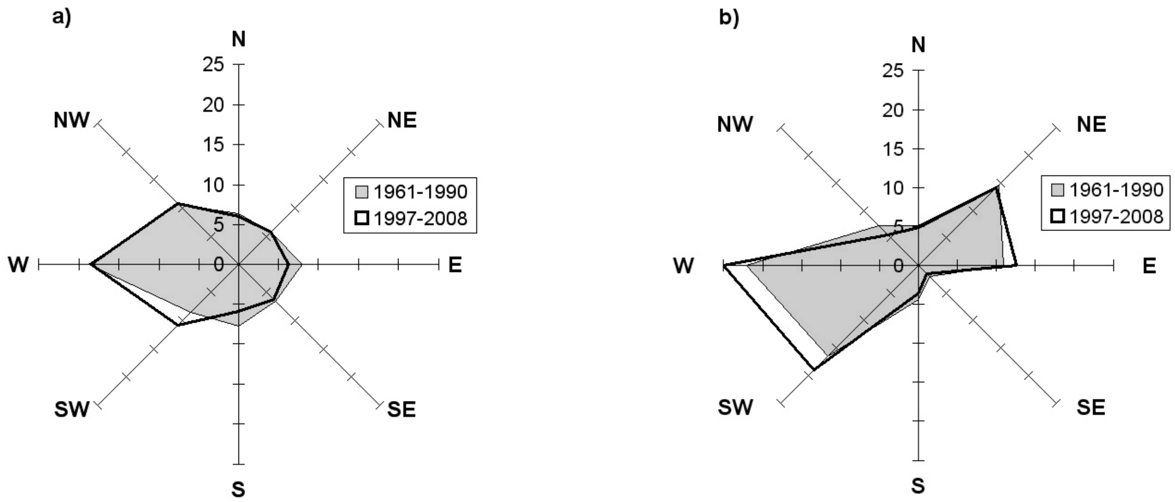

Fig. 9. a) Air mass advection frequency (%) in Kraków 1961-90 and 1997-2008. b) Wind frequency (%) in Kraków 1961-90 and 1997-2008.

References

1. PRINN R.G., WEISS R. F., FRASER P. J., SIMMONDS P.G., CUNNOLD D.M., ALYEA F. N., O`DOHERTY S., SALAMEH P., MILLER B.R., HUANG J., WANG R.H.J., HARTLEY D.E., HARTH C., STEELE L.P., STURROCK G., MIDGLEY P.M., MCCULLOCH A. A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. J.Geophys.Res. **105**, (D14), 17751, **2000**.
2. MAISS M.H., BRENNINKMEIJER C. A. M. Atmospheric SF_6, trends, sources and prospects. Environ. Sci. Technol. **32**, 3077, **1998**.
3. SANTELLA N., HO D.T., SCHLOSSER P., STUTE M. Distribution of atmospheric SF_6 near a large urban area as recorded in the vadose zone., Environmental Science & Technology; **37**, 1069, **2003**.
4. SIMMONDS P. G., DERWENT R. G., MCCULLOCH A., O'DOHERTY S., GAUDRY A. Long-term trends in concentration of halocarbons and radiatively active trace gases in Atlantic and European air masses monitored at Mace Head, Ireland from 1987-1994. Atmos. Environ. **30**, 4041, **1998**.
5. RIVETT A.C., MARTIN D., NICKLESS G., SIMMONDS P.G., O'DOHERTY S.J., GRAY D.J., SHALLCROSS D.E. In situ gas chromatographic measurments of holocarbons in an urban environment. Atmospheric Environment, **37**, 2221, **2003**.
6. LASA J., SLIWKA I. Long term measurements of the concentration of holocarbons in an urban area of Kraków, Poland. Applied Energy. **75**, 155, **2003**.
7. The Journal of Laws No. 52, Item 537. The Act of law on proceedings in Poland with the Earth ozone layer depleting substances. Act of 25 May 2001, signed by President of Poland 1.07.**2002**.
8. DARLING W.G., GOODDY D.C. Assessing the applicability of global CFC and SF_6 input functions to groundwater dating in Britain. Science of the Total Environment **387**, 353, **2007**.
9. ŚLIWKA I., LASA J., ZUBER A., OPOKA M., JACKOWICZ-KORCZYNSKI M. Headspace extraction method for simultaneous determination of SF_6, CCL_3F, CCL_2F_2 and CCL_2FCCLF_2 in water. Analytical Chemistry (Warsaw); **49**, 535, **2004**.
10. HO DT., SCHLOSSER P., SMETHIE W.M., SIMPSON H.J. Variability in atmospheric chlorofluorocarbons (CCl_3F and CCl_2F_2) near a large urban area: Implications for groundwater dating. Environmental Science & Technology; **32**, 2377, **1998**.
11. LASA J., SLIWKA I. Stability examination of the response of a GC equipped with an ECD working in a constants current mode. Anal. Chem. (Warsaw) **46**, 421, **2001**.
12. SLIWKA I., LASA J. A method for improvement of precision and accuracy in concentration measurements based on external standard. Anal. Chem. (Warsaw) **47**, 1, **2002**.
13. http://agage.eas.gatech.edu/
14. TAYLOR J. R. An Introduction to Error Analysis, Oxford University Press. **1982**.